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A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

Annual Summary Report for the Period
April 4, 1963 to April 3, 1964

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To

GEORGE C. MARSHALL SPACE FLIGHT CENTER
National Aeronautics and Space Administration
Huntsville, Alabama

SOUTHERN RESEARCH INSTITUTE
2000 9th Avenue S. Birmingham 5, Alabama

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Project 1259, Report 38

Robert E. Burks, Jr.
Thomas W. Ray
Organic Section

Contract NAS 8-1510

Southern Research Institute
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FOREWORD

This report was prepared by Southern Research Institute under Contract NAS8-1510, "A Study of Polymers Containing Silicon-Nitrogen Bonds," for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Materials Branch of the George C. Marshall Space Flight Center with Mr. James D. Byrd acting as project engineer.

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A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

I. INTRODUCTION AND STATUS

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Silicon-nitrogen compounds are being investigated as a source of materials that are needed for advancing space and aviation technology. New liquids and plastics are needed for sealants, lubricants, coatings, heat barriers, hydraulic fluids, elastomers, potting compounds, and structural plastics that can be used at extremes of temperature and in intense radiation fields at low pressure. This report covers the fourth year of the study. The preceding work was covered in three annual reports.[1,2,3]

At the start of the present year's work, a large amount of information had been obtained on the ability of silicon-nitrogen compounds to polymerize, to endure thermal stress, and to resist chemical action. Encouraging data had been obtained on several different classes of silicon-nitrogen polymers. During the past year the work was extended, and substantially better materials were developed for coatings and elastomers. Improvements were made in the thickness, flexibility, and thermal endurance of protective coatings on metals and in the toughness and thermal endurance of elastomers. An improvement was made in the method of carrying out the reaction of chlorosilanes with ammonia. In addition, a number of routes to polymers were studied and rejected as being of relatively little value.

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II. DISCUSSION OF RESULTS

A. General Aspects of Silicon-Nitrogen Chemistry

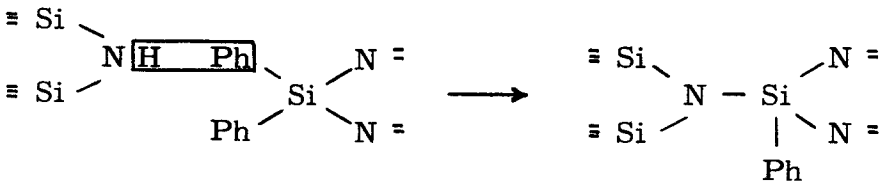
Our research on silicon-nitrogen compounds has been conducted along two lines. One has been to study silicon-nitrogen compounds and polymers, as such; the other has been to study the use of silicon-nitrogen compounds as starting materials for producing end products with properties that are not obtainable by other means. These two lines of research have been followed simultaneously. The most promising end products have been those in which the Si-N groups have been partially converted to Si-O groups, and it appears that materials containing both Si-N and Si-O groups have some special qualities that do not exist in previously known materials. These qualities may result, at least in part, from the reaction of Si-N groups with the oxide surfaces of metals to provide exceptional adhesion. The advantages relative to siloxane compounds may also result, in part, from the cross-linking that is possible through the trivalent nitrogen but not through the divalent oxygen.

Silylamines react with hydroxy compounds in this manner:

$$\equiv Si - \overset{R}{\underset{|}{N}}H + HO - R' \longrightarrow \equiv Si - O - R' + RNH_2$$

This type of reaction may occur between silylamines and oxides or hydroxides on the surfaces of metals or on the surfaces of ceramics and may account for the excellent adhesion of silylamine coatings. The corresponding reaction could occur with siloxanes and silanols, but only with much greater difficulty. The reaction of difunctional silylamines with difunctional hydroxyaromatic compounds, which was first used at the Marshall Space Flight Center, has been used in our studies to form silicon-oxygen-aromatic polymers with high molecular weights. Similar products with such high molecular weights have not been obtained by other methods.

Another advantage of silylamines over siloxanes lies in the following reaction which occurs during heating:

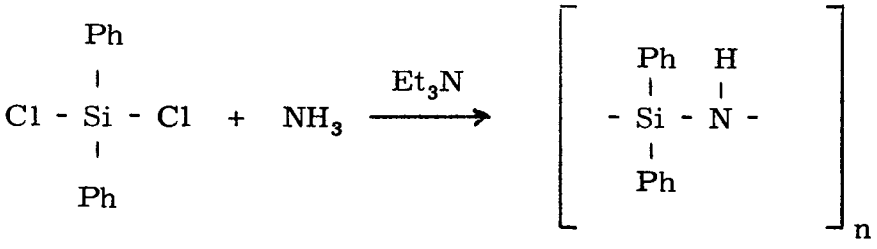


The product has a high degree of stability to heat, moisture, and acids. Siloxanes cannot undergo a corresponding reaction.

The possible usage of silicon-nitrogen compounds as starting materials for producing polymers not obtainable by other methods greatly enlarges the opportunities for developing useful new products.

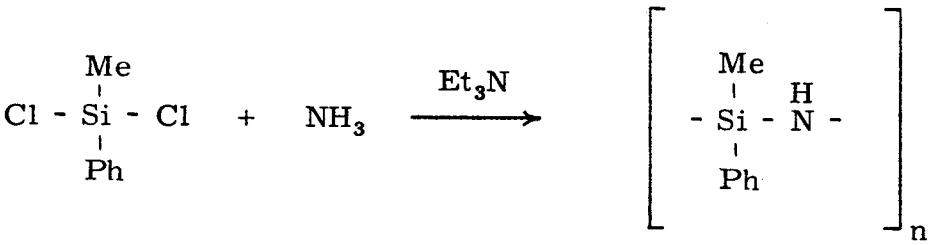
B. Specific Studies of the Past Year

Tertiary amines were found to have a beneficial effect in preventing cyclization and permitting linear polymerization. The tertiary amines apparently alter the spatial configurations of chlorosilanes, thereby retarding cyclization and promoting linear polymerization. The presence of triethylamine in a reaction of diphenyldichlorosilane with ammonia largely prevented the formation of hexaphenylcyclotrisilazane; however, high polymers were not formed. The value of n



diphenylsilyl amine
("polymeric diphenyl silazane")

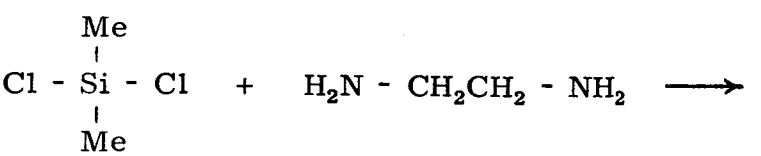
in the polymeric diphenyl silazane was only about 4, but the entire product had excellent coating properties, whereas hexaphenylcyclotrisilazane forms relatively poor coatings because of brittleness. Triethylamine was also helpful in producing a promising coating agent from the reaction of methylphenyldichlorosilane with ammonia.



methylphenyl silazane

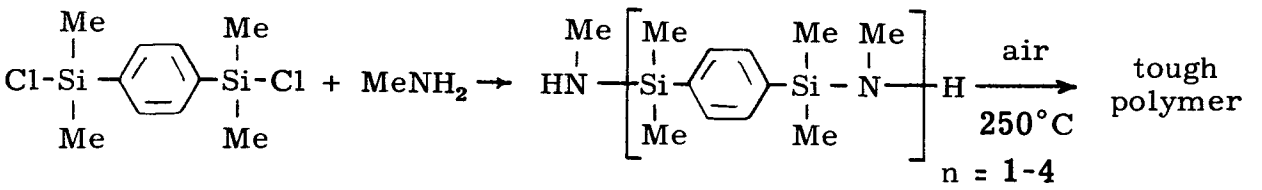
Methylphenyl silazane coatings 6-8 mils thick remained intact on aluminum when they were cooled after being heated at 400°C for 5 hours in air. Coatings 0.5-1 mil thick on aluminum remained intact when they were cooled and bent after 20 hours at 400°C in air.

Two new types of resilient polymers with excellent stability at high temperatures were made in the past year. One type was made from the methylphenyl silazane described above and a dimethylsilyl derivative of ethylenediamine.



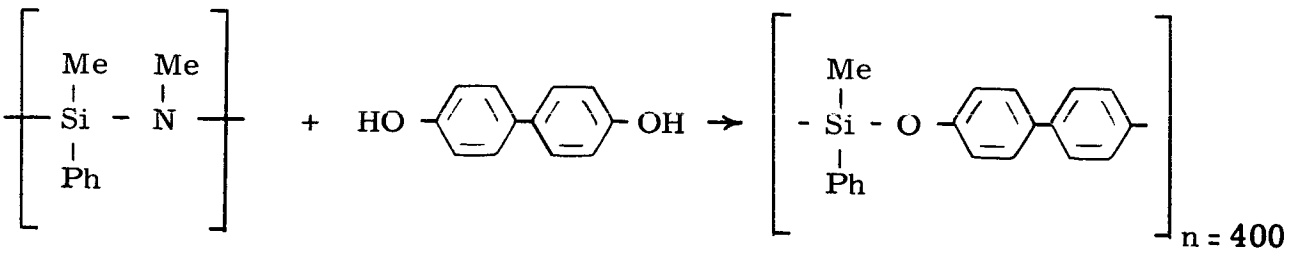
mixed linear and cyclic structures of molecular weight 1000-2000.

A non-foamed sheet of the polymer remained flexible and resilient after 2.25 hours at 400°C. Although the polymer had very little strength, its thermal stability was extraordinary. It may be useful in gaskets with glass cloth or asbestos as reinforcement. The other type of resilient polymer was made by heating the product of the reaction of methylamine with 1,4-bis(dimethylchlorosilyl)benzene.



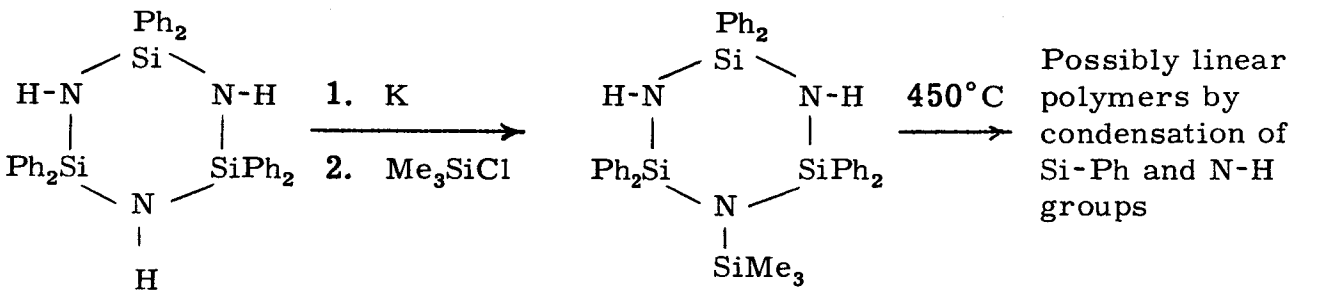
The polymer was tough, and it was resilient after 30 minutes at 400°C.

A type of reaction first studied at George C. Marshall Space Flight Center was used also in this project to make silicon-oxygen-aromatic polymers from methylphenyl methylamino silazane. They have promising properties as coating agents, structural plastics, and adhesives.



Lap joints made between strips of aluminum or stainless steel with the polymer as adhesive had strengths of 4000-5000 psi after being cured at 300-400°C.

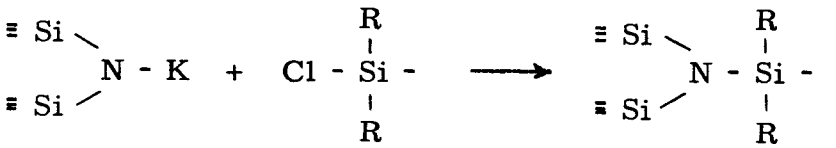
An N-trimethylsilyl derivative of a cyclic silazane that would have a functionality of only two, and that, therefore, should tend to form linear rather than cyclic polymers was investigated.



The desired trimethylsilyl derivative was synthesized, but only with considerable difficulty because of disproportionation. Polymerization evidently occurred at 450°C, but it was accompanied by reactions of the trimethylsilyl groups, and brittle solids were formed.

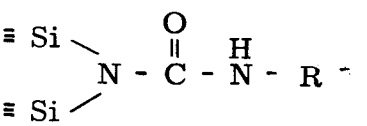
The curing temperatures of some silylamine coating agents were reduced by adding small amounts of silylamines with silicon-hydrogen bonds, which were made by the reaction of methylhydrogendichlorosilane with ammonia. Brittleness was also increased, probably as a result of increased cross-linking.

The alkali derivatives of cyclic silazanes were tried unsuccessfully as routes to polymers.



The N-K and Cl-Si groups did not react readily, and the temperatures required for reaction also caused rearrangement and disproportionation.

The reactions of isocyanates with cyclic silazanes were studied, because isocyanates offered a possibility for making polymers of cyclic silazanes connected by urea groups



The stability of amide linkages in silicon-nitrogen compounds was not known, and it seemed possible that they would be relatively stable to moisture. The desired products were not obtained; the isocyanate opened the silazane ring and reacted with the fragments in a manner that was too complex for simple formation of linear polymers. The products that were obtained were not particularly stable to heat.

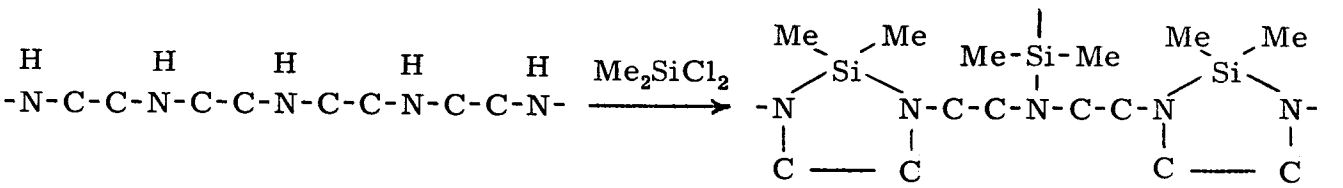
Aluminum hydroxide and aluminum ethoxide reacted with silylamines to form polymers, but they were brittle. Although no method was found to reduce the brittleness, the reaction may possibly be useful for curing silylamine polymers.

Several attempts were made to form silicon-nitrogen polymers by reactions between silylamines and silicon ethoxides, which are esters of silicic acids. This reaction would be analogous to the formation of amides by treating carboxylic esters with amines. It would be highly desirable to form silylamines by this method to avoid the necessity of disposing of the hydrochloric acid that is produced when amines are added to chlorosilanes. The silicon esters did not react to an appreciable extent with silylamines even in the presence of acidic or basic catalysts.

The dimethylsilyl derivative of ethylenediamine, "ethylenediamine silazane," was studied in an effort to polymerize it further or to improve its utility when mixed with other materials. It has been valuable in the past as a plasticizer or curing agent for other silylamines. It also was converted to the only elastic material of this project that has remained resilient at -80°C. The additional studies did not result in the production of satisfactory polymers with ethylenediamine silazane as the major component, but a treatment with bis(methylamino)diphenylsilane did improve its properties as a plasticizer slightly.

Measurements of the heats of combustion of silazanes were investigated as a means of obtaining significant data to indicate the strength of Si-N bonds. Such data would contribute to a better understanding of thermal properties and opportunities for future development. It was especially desirable to compare linear and cyclic silazanes, but complete combustion of the compounds could not be obtained even though several methods were tried. Evidently others have encountered similar difficulties with siloxanes. Accurate determinations of heats of combustion appear to be difficult because the compounds are not only highly stable but the heats of combustion are low.

Attempts to silylate polyethylenimine to form a silicon-nitrogen polymer were not successful. The effort was undertaken, because this route seemed to offer an opportunity for forming silicon-nitrogen polymers of high molecular weight with occasional cross-links. If the reaction had been successful, the product might have been a silicon-nitrogen elastomer of the following type:



An attempt was made to form a polymer by treating phthalocyaninodichlorosilane with ammonia. If a polymer were formed by this reaction, it would probably have exceptional thermal stability. The reaction was suggested, because the large size and shape of the phthalocyanine group would have a tendency to prevent cyclization. Phthalocyaninodichlorosilane was treated with ammonia under pressure at 120°C for 64 hours, but no evidence of reaction was found. Evidently the Si-Cl bond is relatively unreactive in the phthalocyanine compound.

III. THE INFLUENCE OF TERTIARY AMINES ON THE AMMONIA-CHLOROSILANE REACTION

A. Discussion

1. The role of tertiary amines

Tertiary amines have been found to have a beneficial effect on the formation of linear polymers in the reaction of chlorosilanes with ammonia, but, so far, no high polymers have been formed. The products obtained were, however, significantly better as coating agents and as starting materials for elastomers than the corresponding materials obtained without the tertiary amine. The explanation probably lies in a sizable reduction in the amount of cyclization during the ammonia-chlorosilane reaction. It is now desirable to find a method of extending the beneficial effect of the tertiary amines.

The study of the effect of tertiary amines was initiated by consideration of the effect of coordination on silicon tetrafluoride. Silicon tetrafluoride has a tetrahedral structure. Attachment of other groups to the SiF_4 molecule by coordination through the d-orbitals produces a bipyramidal molecule in which either three or four fluorine atoms are planar.[4] Doubtless, coordination affects the spatial arrangement of the halide atoms. Chlorosilanes are also known to form stable complexes with tertiary amines.[4]

Formation of high molecular weight silazane polymers by the ammonia-dichlorosilane reaction has failed, largely because the growing chains cyclize when the number of Si-N units is 4 or less.

$$R_2SiCl_2 + NH_3 \longrightarrow \left[- \underset{\displaystyle R}{\overset{\displaystyle R}{\overset{|}{\underset{|}{Si}}}} - \overset{\displaystyle H}{\overset{|}{N}} - \right]_{n = 2\text{-}4}$$

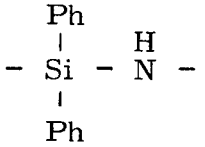
Any factor that tends to force the halide atoms into a linear configuration should inhibit cyclization, and, therefore, the influence of triethylamine on the reaction of diphenyldichlorosilane with ammonia was tried. Without triethylamine, the reaction produced hexaphenylcyclotrisilazane in about 75% yield.[5] With triethylamine, the formation of hexaphenylcyclotrisilazane was drastically reduced. The total yield of polymer was 90-95% of theory, and crystals of hexaphenylcyclotrisilazane appeared only after prolonged standing at room temperature after the triethylamine was removed. It was apparent that cyclization had been markedly inhibited by the triethylamine.

Pyridine was also tried as an inhibitor of cyclization in the reaction of diphenyldichlorosilane with ammonia, but it was much less effective than triethylamine. Evidently, the basicity of the nitrogen atom and the size of the tertiary amine molecule are significant factors.

The reaction was also studied at high and low temperatures. At a low temperature, 1-10°C, the reaction proceeded in about the same way that it did at 25-55°C with no attempt to control the temperature. At a high temperature, 125-143°C, with tributylamine, the yield of crystalline material was about 20%, which showed that an appreciable amount of cyclization had occurred. Polymers of high molecular weight were not produced at either temperature range.

2. Studies of polymeric diphenylsilazane (prepared with triethylamine) as a coating agent

Before the beneficial effect of triethylamine was known, the Si-N coating agent that was the most promising for practical use was the resinous by-product obtained in 19% yield in the preparation of hexaphenylcyclotrisilazane[5] from diphenyldichlorosilane and ammonia. By running the same reaction in the presence of triethylamine, the yield of product useful for coatings was increased to 90% or more, and it was not necessary to remove the hexaphenylcyclotrisilazane. The product made in the presence of triethylamine is called "polymeric diphenylsilazane." It and the hexaphenylcyclotrisilazane by-product are believed to be low molecular weight polymers with this repeating unit:



Both the hexaphenylcyclotrisilazane by-product and the polymeric diphenylsilazane form protective coatings of good stability when heated alone. However, they form more flexible coatings when heated with 10% by weight of ethylenediamine silazane. Such coatings require curing at 300°C or higher.[5] They are flexible and still protect an aluminum substrate from hydrochloric acid after being heated in air at 400°C for 18 hours. Data on the performance of the various products in coatings are given in Table I. It appears that the best coating agent was obtained from the reaction at 1-10°C when the mole ratio of triethylamine to diphenyldichlorosilane was 2:1. However, it is desirable to examine the effects of reaction variables further before reaching a conclusion.

Additional studies of coating agents prepared by the reaction of methylphenyldichlorosilane with ammonia in the presence of triethylamine are described in Section IV.

3. Attempts to polymerize nonamethylcyclotrisilazane

The question of whether cyclic silazane rings could be opened to form linear polymers was re-examined after it was learned that tertiary amines favor linear polymerization. It is desirable to obtain fully methylated silazane polymers, because nonamethylcyclotrisilazane, which is a fully methylated cyclic silazane, is known to have fair hydrolytic stability and outstanding thermal stability.[6] Therefore, the polymerization of nonamethylcyclotrisilazane was studied by an equilibration technique that was similar to the methods used to prepare high polymers from cyclic siloxanes.[7]

Tetramethylammonium chloride was tried as the catalyst, because it contains no NH groups, which can serve as sources of unmethylated nitrogen atoms by an exchange process. Tributylamine was tried as the complexing agent because of its high boiling point. Reactions were tried with nonamethylcyclotrisilazane alone and with an equimolar mixture of carefully purified nonamethylcyclotrisilazane and bis(methylamino)diphenylsilane. It was postulated that bis(methylamino)diphenylsilane might facilitate polymerization by reacting with free-radical ends of opened nonamethylcyclotrisilazane rings, thereby preventing recombination of the original rings. The reactions were run at 100°C and 215°C for 40 hours.

Table I. Performance of Polymeric Diphenylsilazanes in Coatings on Aluminum.

		Different Preparations of Polymeric Diphenylsilazane								
		Different ratios of Et_3N : Ph_2SiCl_2			Different reaction temps.		Different pretreatments			
	HPCTS by-product[a]	15:1[b]	2:1[c]	1:1[d]	25-55°C[e]	1-10°C[f]	None[f]	Boiled[g]	Extract[h]	EDS added[j]
Amount applied per 15 cm^2, mg	35	35	35	35	17	17	17	17	17	17
Heat exposure										
Time, hr	16	16	16	16	18	18	18	18	18	18
Temp, °C	400	400	400	400	370	370	400	400	400	400
Amount remaining, %	22	10	50	18	39	48	27	16	29	52
Approximate thickness, mils	0.2	0.2	0.4	0.2	0.3	0.4	0.2	0.2	0.3	0.4
Appearance	clear, smooth	clear, smooth	cloudy, uneven	cloudy, smooth	cloudy, smooth	cloudy, smooth	cloudy, smooth	clear, uneven	cloudy, uneven	clear, smooth
Protection against 19% HCl										
Unbent	good	good	good	good	good	good	good	poor	good	good
Bent	poor	poor	poor	poor	poor	good	fair	poor	poor	very good

[a] Hexaphenylcyclotrisilazane by-product prepared by method of reference 5 in bibliography.

[b] Described in Section III. B. 1. a. second reaction, triethylamine as solvent.

[c] Described in Section III. B. 1. a. first reaction.

[d] Described in Section III. B. 1. a. third reaction.

[e] Described in Section III. B. 1. b. first reaction.

[f] Described in Section III. B. 1. b. second reaction.

[g] Polymeric diphenylsilazane (f) boiled 5 minutes at about 400°C.

[h] Polymeric diphenylsilazane (f), ether-soluble portion.

[j] Polymeric diphenylsilazane, 9 parts; ethylenediamine silazane (EDS), 1 part. Method of preparing EDS in reference 9 of bibliography.

The amounts of the polymers obtained in the reactions of nonamethylcyclotrisilazane alone were less than 5% of the total product, and the highest molecular weight of any product was 1450. In the reactions that contained bis(methylamino)diphenylsilane, 20-30% of the reactants polymerized and had a molecular weight of 850. However, bis(methylamino)diphenylsilane is known to polymerize even when heated alone.

It was evident that these reactions did not result in a significant amount of linear polymerization by opening of rings; the silazane ring apparently was too stable to open under the reaction conditions.

B. Experimental Details

1. Preparation of polymeric diphenylsilazane

a. With various amounts of triethylamine

In the first reaction, 2 moles of triethylamine were used for each mole of diphenyldichlorosilane. In a 1-liter, 3-neck, round-bottom flask fitted with a stirrer, dropping funnel, reflux condenser, and gas-inlet tube were placed 300 ml of benzene and 39.05 ml (28.23 g, 0.279 mole) of triethylamine that had been purified by distillation from phthalic anhydride and then from potassium hydroxide. Then 28.90 ml (35.32 g, 0.139 mole) of diphenyldichlorosilane was added dropwise with stirring. The mixture became thick and cloudy. Ammonia was passed over the surface of the mixture for 2.5 hours as it was being stirred. The temperature rose to 40°C, and returned to room temperature. After the mixture had stood overnight, the Beilstein Test for halogens was positive; so introduction of ammonia was resumed for 2 hours. Finally, the mixture was heated to 80°C with stirring and then allowed to cool. The salts were removed by centrifugation, and the solid was washed with benzene. The solvent was removed by distillation at the reduced pressure provided by a water aspirator; the final pot temperature was 87°C. The cloudy, tan, viscous product weighed 25.9 g, which was 94.1% of the theoretical yield, if $-Si(Ph)_2NH-$ was the formula of the product. The molecular weight as determined by vapor osmometry was 440 (average of 438 and 440).

In a second reaction, triethylamine was used as the solvent. Diphenyldichlorosilane, 35.32 g (0.140 mole) was added to 300 ml (216.9 g, 2.14 moles) of triethylamine, and ammonia was passed in as described above. The yield was 25.8 g, 93.7% of theoretical, if $-Si(Ph)_2NH-$ is assumed to be the formula of the product. The molecular weight as determined by vapor osmometry was 570 (average of 563 and 577).

In the third reaction, the mole ratio of chlorosilane to tertiary amine was 1:1. Diphenyldichlorosilane, 35.32 g (0.140 mole) was added to 19.52 ml (14.11 g, 0.140 mole) of triethylamine in 300 ml of benzene, and then the ammonia was passed in as before. The yield was 27.1 g, 98.4% of theoretical, if $-Si(Ph)_2NH-$ is assumed to be the formula of the product.

The products of these three reactions were compared in coatings as described in Section III. B. 1. d. and summarized in Table I.

b. With triethylamine at different reaction temperatures

The first reaction was run with no attempt to control the temperature. Diphenyldichlorosilane, 28.90 ml (35.32 g, 0.139 mole) was added to 39.05 ml (28.23 g, 0.279 mole) of triethylamine in 300 ml of benzene. The mixture was slightly cloudy. It was stirred while dry ammonia was passed over the surface for 5 hours. The temperature rose to 55°C. The solution was allowed to stand overnight, then it was centrifuged to remove the salt, and the benzene was distilled off, finally at reduced pressure. The product was 25.0 g of a tan, slightly viscous liquid. This represents 91% yield, if the formula is assumed to be $-SiPh_2NH-$.

A second reaction was run at a lower temperature with the same materials as used in the reaction described above except that the solvent was toluene. The addition of ammonia was started with the solution at 1°C, and the temperature was allowed to rise to 10°C. In 30 minutes, the reaction rate had decreased, and the temperature was held at 2°C for 105 minutes. The mixture was allowed to stand overnight at room temperature under an atmosphere of ammonia as maintained by a balloon, then it was warmed to 90°C to boil off the ammonia. The resulting solution was filtered, and the toluene was distilled off. The product was a cloudy, colorless, viscous liquid that weighed 25.1 g. The yield was 91% of theory, if the formula is assumed to be $-SiPh_2NH-$. Two small portions of the product were treated further to prepare samples for evaluation in coatings. One was boiled for 5 minutes in a test tube over a burner. The other was stirred with 10 volumes of ether, and the ether-soluble portion was evaluated. Neither of these treatments constituted an improvement, as discussed below in Section III. B. 1. d.

A third reaction was run at an elevated temperature as follows: Diphenyldichlorosilane, 28.90 ml (35.32 g, 0.139 mole) was added with stirring to 300 ml (233.5 g, 1.26 mole) of tri-n-butylamine that had been distilled from phthalic anhydride and then from potassium hydroxide. The solution was cloudy. Heat was applied, and at 115°C the cloudiness disappeared. At 136°C, ammonia was introduced, and the temperature rose to 143°C. In 30 minutes, the temperature dropped to 125°C, and heat was applied to keep it at 125°C for 3 hours while the atmosphere of ammonia was maintained. The mixture was allowed to stand overnight under an atmosphere of ammonia. The product was isolated by centrifugation and distillation of the tributylamine at reduced pressure. The product was a white, semi-crystalline, viscous mixture. The crystalline portion, 5.01 g, was separated by dissolving the viscous liquid in Skellysolve "B". The crystals melted over a range of 189-215°C. Evidently they were crude hexaphenylcyclotrisilazane, obtained in 20.5% yield.

c. With pyridine

Pyridine was purified for trial as an agent to inhibit cyclization by distilling it first from phthalic anhydride and then from potassium hydroxide. Diphenyldichlorosilane, 28.9 ml (35.32 g, 0.140 mole), and pyridine, 300 ml (294.6 g, 3.85 moles), were mixed to form a homogeneous liquid, then ammonia was passed over the surface of the mixture for 3.5 hours. The temperature rose to 55°C. After the mixture had stood overnight, the Beilstein Test for halogens was negative in the supernatant liquid. The mixture was refluxed at 115°C for 1.5 hour, then it was centrifuged to remove salt and distilled to remove the pyridine. The residue, 27.6 g, was a brown, semi-crystalline solid. Recrystallization from benzene yielded 20.58 g of solid that melted from 185-209°C in the various fractions. Evaporation of the mother liquors yielded 7.0 g of a dark, sticky, semi-solid residue that did not perform well in coatings on aluminum.

d. Performance of coatings made from polymeric diphenylsilazanes

Coatings were made with the various polymeric diphenylsilazanes and evaluated with results as given in Table I. Solutions of the polymers were prepared at 10% or 20% concentrations in benzene. The solutions were spread on aluminum panels over an area of 15 cm^2 on each. After each panel was heated for 1 hour at 175°C, it was exposed to 375°C or 400°C as indicated in Table I. The panel was then bent to a radius of curvature of about 6 mm and immersed in 19% hydrochloric acid until the uncoated areas were deeply etched. The acid treatment revealed whether the coating had cracked or peeled.

A coating was also prepared by mixing polymeric diphenylsilazane, 9 parts, with ethylenediamine silazane (EDS), 1 part, and dissolving the mixture in benzene to form a 10% solution for application. The polymeric diphenylsilazane was the one made at 1-10°C with a 2:1 mole ratio of triethylamine to diphenyldichlorosilane as described in Section III.B.b. The EDS was prepared from commercial ethylenediamine (Union Carbide Chemicals Company) as described previously.[9] The advantage of adding EDS was demonstrated again, as shown by the data of Table I.

2. Attempts to polymerize nonamethylcyclotrisilazane

The nonamethylcyclotrisilazane used in the polymerization experiments was prepared by the method described previously.[10] It melted at 33.5°C. The bis(methylamino)diphenylsilane was prepared by the method of Larsson.[11] It boiled at 136-137°C at 1 mm pressure.

The first attempt at polymerization of nonamethylcyclotrisilazane in the presence of an amine was conducted as follows: In a 100-ml, 3-neck flask fitted with a magnetic stirrer, reflux condenser, and thermometer were placed 16 grams (0.0612 mole) of nonamethylcyclotrisilazane, 27 grams (0.127 mole) of tributylamine, and 0.63 gram (0.00575 mole) of tetramethylammonium chloride. The mixture was refluxed for 40 hours at 216°C. Every 8 hours a 2-ml sample was withdrawn. After being centrifuged to remove solids each sample was placed in a vacuum desiccator and held at pressures less than 0.1 mm of Hg for 40 hours. The weight of the residue remaining from each sample was determined with the expectation that weights could be used as a measure of the amount of high molecular weight material formed. These weights did give an indication of polymerization, but the precision of the method was not sufficient to provide significant numerical values.

The material that remained in the reaction vessel after 40 hours of reflux was distilled at 1.0 mm of Hg until the pot temperature reached 60°C. At this point only a small amount, 0.5 g (4% yield) of a brown, viscous liquid remained. The molecular weight of this material was determined by vapor osmometry to be 1420-1455.

The same experiment was repeated except the temperature was held at 100°C with no reflux. The samples taken at 8-hour intervals indicated no formation of high molecular weight material, and there was only a trace of residue left after distillation. Apparently, the silazane ring was not ruptured at 100°C.

An attempt to polymerize nonamethylcyclotrisilazane and bis(methylamino)diphenylsilazane was conducted as follows: In the same apparatus previously described were placed 9.0 grams (0.0344 mole) of nonamethylcyclotrisilazane, 8.5 grams (0.0351 mole) of bis(methylamino)diphenylsilane, 27 grams (0.127 mole) of tributylamine, and 0.69 grams (0.0063 mole) of tetramethylammonium chloride. The mixture was refluxed 40 hours at 213°C, and 2-ml samples were withdrawn every 8 hours. Each sample was centrifuged to remove amine hydrochloride and then evaporated at low pressure to obtain the polymer. However, the evaporation was unsatisfactory because of the difficulty of deciding when evaporation was complete, and so useful data were not obtained.

After the reaction had been run for a total of 40 hours, the remaining liquid was distilled at 1 mm pressure until the pot temperature reached 280°C. The sticky residue that remained weighed 2.5 grams (20% yield) and had a molecular weight of 555.

The experiment was repeated with identical conditions except the temperature was held at 100°C. Four grams (30% yield) of sticky material was obtained. It had a molecular weight of 845.

IV. POLYMERIZATION OF METHYLPHENYLSILYL AMINES

A. Discussion

The study of methylphenylsilyl amines was resumed, because earlier work[12] had indicated that the methyl group imparted some flexibility to coatings without significantly decreasing the stability below that of the diphenylsilyl compounds.

1. Polymers made with the aid of triethylamine

Coatings and resilient polymers were made by curing methylphenyl silylamines in air. The methylphenyl silylamines were made by the reaction of methylphenyldichlorosilane with ammonia. The toughness of the polymers subsequently prepared was significantly improved when triethylamine was used in the ammonia-chlorosilane reaction. The initial product of the reaction of methylphenyldichlorosilane with ammonia is a mixture of methylphenyl silylamines that have the silazane structure. It is called "methylphenyl silazane." The similar material made in the presence of triethylamine is called "methylphenyl silazane-TEA." The cured materials were resilient only when the methylphenyl silazane, made with or without triethylamine, was mixed with ethylenediamine silazane (EDS).[9]

a. Coatings

Coatings 6-8 mils thick made by curing methylphenyl silazane-TEA on aluminum remained in place without crazing for 5 hours at 400°C. A coating that varied from 0.8 to 1.5 mils thick was heated 20 hours at 400°C, and then it was bent to a 4-mm radius of curvature. It cracked very slightly in the thickest portion (1.5 mil) but nowhere else. About 50% of the applied prepolymer remained in the 0.8 to 1.5-mil coating after being heated 20 hours at 400°C.

Coatings were also made from methylphenyl silazane-TEA pigmented with aluminum, titanium dioxide, and ferric oxide. Pigmentation reduced the flexibility and adhesion appreciably. A coating 1 mil thick with titanium dioxide pigment remained flexible after being heated 7.5 hours at 400°C, but it was no longer flexible after 17.5 hours at 400°C. Results with aluminum and ferric oxide were similar.

In previous work, little or no difference has been seen in the performance of coatings of Si-N on aluminum or stainless steel. The coating of mild steel is a distinctly more difficult problem, however. A coating 6-8 mils thick made from methylphenyl silazane-TEA on mild steel remained intact for 4.5 hours at 400°C in air. After another 0.75 hour of heating at 400°C the coating cracked when cooled. A coating 1 mil thick on mild steel was heated at 400°C for an hour and then cooled by being dropped into water. It was reheated and quenched similarly five times with no evidence of crack formation. On the sixth quench one small crack appeared. The coatings were impervious to 19% hydrochloric acid for about 5 minutes; long enough to cause the uncoated metal to be deeply etched. The limit of endurance of the coating to acids was not determined.

b. Resilient polymers

A mixture of methylphenyl silazane-TEA, 9 parts, and EDS, 1 part, cured in a thin film in air in a Teflon mold formed a flexible, slightly elastic film. The thickness varied from 1-2 mm. It was further heated for 2.25 hours at 400°C, and it remained flexible and resilient. The tensile strength was 116 psi and the elongation at break was 75-100%, according to measurements made at Marshall Space Flight Center. Although the strength was low, the retention of resilience for 2.25 hours at 400°C was noteworthy. This material may be useful in gaskets where the needed strength may be supplied by other materials, such as asbestos or glass fibers. Analyses for nitrogen revealed that the film, after being heated in air for 2.25 hours, contained 2.5-3.5% nitrogen. This amount of nitrogen was about 28% of the original nitrogen present, and it is believed to have a significant role in the formation and properties of the elastic polymer. Exposure of the heated polymer to 30 million roentgens of gamma radiation caused no change that was detectable by handling.

2. Polymers made without triethylamine

The work on methylphenyl silazane prepared without TEA will not be discussed in detail, because the similar silazane made with TEA appears to be of greater interest. However, the experiments made with the former material are described below.

An effort was made to obtain better properties in the methylphenyl silylamines by forming silylamines with N-methyl groups. When methylphenyldichlorosilane was treated alternately with methylamine and ammonia, the product contained N-methyl and N-hydrogen groups in a ratio of approximately 15:100. Evaluation of the material in coatings revealed no outstanding properties in regard to flexibility or thermal stability. When methylphenyldichlorosilane was treated with a mixture of methylamine and ammonia, the methylamine did not react.

Treatment of methylphenyldichlorosilane with methylamine alone produced a yellow, cloudy liquid. In an attempt to increase the degree of polymerization, the liquid was heated at 160-170°C with ammonium chloride, which is known to be a catalyst for rearranging Si-N bonds. The viscosity of the liquid increased slightly, but no significant amount of polymerization was obtained. The product formed brittle coatings that adhered poorly to aluminum.

Treatment of methylphenyldichlorosilane with aniline produced a dark-colored semi-crystalline material. Heating the crude product at 190°C for 64 hours in air produced a fairly tough, resilient polymer that was smooth, homogeneous, and black. It retained some elasticity after 60 minutes at 425°C, whereas Viton A became hard when heated 15 minutes at the same temperature. Attempts to purify the crude compound produced a crystalline material that was probably largely dianilinomethylphenylsilane. However, analysis did not confirm the structure, and so it is called the "methylphenyl anilino silazane." Heating the purified product in air did not polymerize it satisfactorily. Heating it with aluminum ethoxide produced a brittle polymer. The resilient polymer made by heating methylphenyl anilino silazane at 190°C seems worthy of additional investigation because of its toughness and thermal stability.

B. Experimental Details

1. Methylphenyl silazane-TEA

a. Preparation

In a 1-liter, 3-neck flask equipped with stirrer, reflux condenser, thermometer, and gas-inlet tube were placed 95.5 g (0.5 mole) of methylphenyldichlorosilane, 101.2 g (1.0 mole) of purified triethylamine, and 600 ml of benzene. The solution was stirred for 30 minutes. Ammonia, after being dried over sodium, was passed over the stirred solution for 4 hours. The temperature was kept below 25°C during the addition. After the addition of the ammonia, the reaction was refluxed for 3 hours. The salt was filtered off, and the benzene and triethylamine were distilled from the reaction. The product was 66.7 g of a cloudy, viscous liquid. This liquid is called "methylphenyl silazane-TEA."

b. Properties as coatings

Methylphenyl silazane-TEA was boiled in a test tube for 8-10 minutes during which time it became a very viscous, sticky liquid. The molecular weight of the viscous liquid, as determined by vapor osmometry, was 645 (average of 640 and 647). It was applied to an aluminum panel and heated at 400°C for 5 hours without cracking or discoloration; however, after longer heating at 400°C, the 6 to 8-mil coating crazed when the panel was bent. The best time and temperature for curing have not been determined. Similar coatings did not become hard in 19 hours at 190°C. However, heating for 3 hours at 350°C produced hard, transparent, pale yellow films that adhered well to the aluminum. Other coatings were about 1 mil thick and were prepared by spreading the boiled prepolymer with a doctor blade on a panel that had been warmed to about 50°C. Strips of "Scotch" tape were used at the sides of the area to be coated to adjust the thickness of the coating.

Another coating was made by spreading 0.4 ml of a 20% solution of the boiled prepolymer on aluminum over an area of about 15 square centimeters. The benzene was allowed to evaporate at room temperature, and then the panel was heated 2 hours at 190°C. At this time, the coating did not flow at 190°C, and it could not be scratched with the fingernail at room temperature. It became soft again but did not flow at 400°C. After 20 hours at 400°C the coating varied from 0.8 to 1.5 mils in thickness. Bending the panel to a radius of 4 mm cracked the coating only slightly in the thickest (1.5 mil) portion. The amount of polymer that remained after heating was 55% of that applied.

Aluminum, titanium dioxide, and ferric oxide were incorporated into the boiled prepolymer and the mixtures were evaluated as coatings on aluminum. After trials with different amounts, 10% pigment by weight of the prepolymer was tentatively selected as the preferred amount. A strip of aluminum-pigmented boiled prepolymer was doctored onto an aluminum panel and heated at 190°C for 1 hour, 250°C for 1 hour, and at 400°C for 18 hours. After these heat exposures, the coating was 1.3 mils thick and apparently tightly adhered. It could not be scratched with the fingernail, but after the panel was bent, the bent portion could be scratched easily. A 1-mil coating pigmented with titanium dioxide was prepared by heating the coated panel 1 hour at 190°C, 19.5 hours at 250°C, and 7.5 hours at 400°C. There was no apparent loss of adhesion when the coated panel was bent, but another titanium dioxide-pigmented coating flaked off a panel after 17.5 hours at 400°C. A panel with a 1-mil coating pigmented with ferric oxide was heated at 190°C for 1.75 hours, 250°C for 17 hours, and 400°C for 24 hours. The surface of the coating was rough, and microscopic examination indicated that the roughness was caused by agglomerates of unpigmented polymer. The coated panel was bent after heating without apparent loss of adhesion of the coating.

The experiments with pigments that are described here were selected from a large number of experiments and represent the best results obtained. However, these should be regarded only as exploratory experiments, because the small amount of time assigned to this part of the program did not permit a thorough investigation of different types of pigments, methods of incorporation, and curing schedules.

Coatings of the prepolymer prepared by boiling methylphenyl silazane-TEA were also evaluated on mild steel. The steel panels were cleaned with hydrochloric acid and rinsed with water before the coating was applied. A coating 1 mil thick was applied by doctoring the boiled prepolymer onto a panel heated to 50°C. The panel was heated in air 2 hours at 190°C and 1 hour at 400°C. After being cooled in air, the coating was intact. The panel was then reheated to 400°C and dropped into water. The heating and quenching process was repeated four times without visible signs of cracking of the coating. On the sixth quench, a small crack appeared. Another coating 6-8 mils thick was prepared by spreading the boiled prepolymer onto a warmed panel and then heating at 190°C for 1 hour and 400°C for 4.5 hours. No cracks were visible. Heating was resumed, and a few cracks appeared when the panel was cooled after a total of 5.25 hours at 400°C.

c. Preparation of a resilient polymer

The prepolymer made by boiling methylphenyl silazane-TEA was mixed with EDS[9] in a 9:1 ratio by weight. The mixture was a cloudy, pale yellow, viscous liquid. A small amount of the mixture was poured into a Teflon mold to a depth of about 1 mm and heated 4 days at 190°C. While hot and after being cooled, the product was tacky but did not flow. It was heated further for 2.25 hours at 400°C in air, and then it was a smooth, dark brown, elastic sheet. Measurements made at Marshall Space Flight Center showed that it had an elongation at break of 75-100% and a tensile strength at break of 116 psi. Elemental analyses showed nitrogen contents of 2.5% and 3.6% for samples of slightly different thickness. By calculation the starting material contained 10.9% nitrogen, and so the average of 3.0% nitrogen in the product after heating represents 28% of the original nitrogen. Another sample made in the same manner as the one just described was still resilient after 4.5 hours at 400°C. The polymer that had been heated at 400°C for 2.25 hours was exposed to 30 million roentgens from cobalt-60. No change in its appearance or flexibility was detected by handling.

2. Methylphenyl silazanes made without TEA

a. Preparation of methylphenyl silazane

In a 2-liter, 3-neck flask fitted with a stirrer, reflux condenser, thermometer, and gas-inlet tube were placed 1600 ml of dry benzene and 191.1 g (1.0 mole) of methylphenyldichlorosilane. Ammonia, previously dried over sodium, was passed over the liquid, as it was being stirred for 3 hours; and the resulting mixture was refluxed for 3 hours. The clear supernatant liquid was negative to the Beilstein Test for halogens. The chloride was filtered off and extracted with benzene. The product was isolated by distilling off the benzene, finally at reduced pressure. The pot temperature did not exceed 80°C. The product, "methylphenylsilazane," was a cloudy, viscous liquid that weighed 129.2 g.

Several attempts were made to polymerize the methylphenyl silazane by heating in nitrogen and in air. The results were similar to those that have been obtained with a variety of silazanes. Fibers could be pulled from the melt, but no tough polymers with high softening points were produced. Continued heating finally produced brittle foamed solids with high chemical and thermal stability.

b. Preparation of an elastomer from methylphenyl silazane and ethylenediamine silazane

Methylphenyl silazane was partially polymerized by boiling it in a test tube for 3 minutes. When cool, it was mixed with 10% by weight of ethylenediamine silazane[9] and heated in an oven at 190°C for 18 hours. The product was a non-foamed resilient polymer. When the curing was done in glass, it was difficult to remove the product from the vessel, but it was easily removed from Teflon. The thickest film made was about 1 mm thick.

The resilient polymer was visibly unaffected by acetone, tetrahydrofuran, and aqueous acids and alkalis.

A sample of the resilient polymer and a sample of Viton A were heated in an oven at 190°C for 8 days. Both samples appeared to be unchanged. Then both were heated at 400°C for 2 hours. The heated Viton A crumbled when it was pressed with a spatula, but the heated methylphenyl silazane-EDS polymer still retained most of its original resilience.

A sample of the resilient polymer that had been heated at 450°C for 15 minutes (Sample 3357-15-4) had the elemental composition shown in Table II. Conversion of the mixture of methylphenyl silazane and ethylenediamine silazane to an elastomer evidently eliminated most of the nitrogen.

A sample of glass cloth coated with the methylphenyl resilient polymer formed a flexible, impervious sheet. This type of material could be useful as a gasket for high-temperature applications.

3. Reactions of methylphenyldichlorosilane with ammonia and methylamine

a. Mixture of ammonia and methylamine

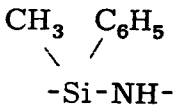
In a 500-ml, 3-neck flask fitted with stirrer, reflux condenser, thermometer, and gas-inlet tube were placed 200 ml of dry benzene and 30 g (0.157 mole) of methylphenyldichlorosilane. Three moles of methylamine and 3 moles of ammonia were mixed and dried over sodium. The mixed vapors were passed over the stirred solution of the silane for 2.5 hours. At the end of this time, the clear supernatant liquid was negative to the Beilstein Test for halogens. The solution was refluxed for 2 hours, cooled, and filtered. The benzene was distilled off leaving 19 g of cloudy, colorless, liquid. The NMR spectrum showed that no N-methyl groups were present.

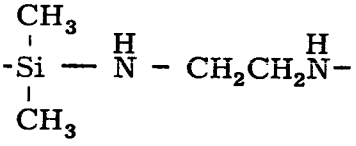
The liquid product was spread on aluminum and heated at 450°C for 30 minutes. The coating remained intact even after the panel was bent and placed in 19%hydrochloric acid until the uncoated areas were badly etched. After being heated at 450°C for longer periods the coating cracked when bent.

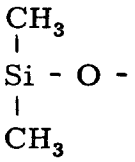
Table II. Elemental Analysis of Elastomer Made from Methylphenyl Silazane

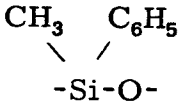
	Found	Calculated			
	Sample 3357-15-4	Formula			
		A	B	C	D
		C_7H_9NSi	$C_4H_{12}N_2Si$	C_2H_6OSi	C_2H_8OSi
Carbon, %	54.11	62.16	41.33	32.39	61.72
Hydrogen, %	6.07	6.70	10.41	8.16	5.92
Nitrogen, %	1.3	10.37	24.10	0	0
Oxygen, %		0	0	21.57	11.74
Silicon, %	23.2	20.77	24.16	37.88	20.62
Remainder, %	15.32				

Formulas

A 

B 

C 

D 

b. Reaction with methylamine and ammonia alternately

To obtain partial reaction of methylphenyldichlorosilane with methylamine, alternate addition of methylamine and ammonia was tried. In a 500-ml, 3-neck flask fitted with stirrer, reflux condenser, and two gas-inlet tubes were placed 250 ml of dry benzene, and 30.0 g (0.157 mole) of methylphenyldichlorosilane. From two separate flasks, ammonia and methylamine were passed over the reaction at the same time for 15 minutes. Then methylamine alone was passed in for 15 minutes followed by ammonia alone for 10 minutes. The alternation was repeated twice more making a total amination time of 1.5 hours. The solution was refluxed for 2 hours, and then the clear supernatant benzene layer was negative to the Beilstein Test for halogens. The precipitate was filtered off, and the benzene was removed by distillation. The product was 18.5 g of a slightly viscous, yellow liquid. The NMR spectrum showed the ratio of N-methyl groups to N-hydrogen groups to be 15:100.

About 4 g of the product was placed in a distilling flask, and half of it was distilled at 378-394°C by heating with a gas flame. Then heavy smoking began, and the effort to distill was discontinued. The undistilled portion undoubtedly had been much hotter than 394°C, but the actual temperature was not determined. It was largely a foamed brittle solid.

Almost the entire product was distilled at 191-203°C at 0.1 mm. The distillate was a cloudy, colorless, viscous liquid that crystallized partially on standing. Attempts to prepare coatings on aluminum by heating thin films in air resulted in very low retention. The films cracked when the panel was bent.

c. Reaction with methylamine alone

Methylphenyldichlorosilane was treated with methylamine by the method described above under IV. B. 2. a. for the reaction with ammonia. The product was a cloudy, yellow, viscous liquid that is called "crude methylphenyl methylamino silazane."

The yellow, viscous crude methylphenyl methylamino silazane was distilled through a 1.2 x 30-cm packed column, and the following fractions were obtained:

Fraction 1. B. p. 67-68°C at 1.5 mm, 2.6 g, clear liquid

Fraction 2. B. p. 68°C at 1.5 mm, 23.4 g, clear liquid

Fraction 3. B. p. 68°C at 1.5 mm, 7.8 g, clear liquid

Fraction 4. Residue, did not distill at 168°C at 1.5 mm; 11.8 g brown solid when cool

Fraction 2 was expected to be bis(methylamino)methylphenylsilane. It did not crystallize at temperatures down to -80°C even when the container in contact with the liquid was scratched with a glass rod. Its neutral equivalent was 95.7 (theoretical, 90.16). Its elemental composition was:

Found: Carbon, 59.87%; hydrogen, 8.08%; nitrogen, 15.79%; silicon, 14.8% (total, 98.54%).

Calculated: Carbon, 59.94%; hydrogen, 8.94%; nitrogen, 15.54%; silicon, 15.58%

The molecular weight of Fraction 2 as determined by vapor osmometry at Galbraith Laboratories, Inc., was 253 (average of 264 and 242); calculated 180.3. These data show that the product was not pure bis-(methylamino)methylphenylsilane. Therefore it is called simply "methylphenyl methylamino silazane."

A sample of the methylphenyl methylamino silazane, 4.0 g, was stirred in a nitrogen atmosphere with 0.1 g of ammonium chloride at 160-170°C for 7 hours. No increase in viscosity was observed. Then another 0.1 g of ammonium chloride was added, and heating was continued for 7 hours. The final product was only slightly more viscous than at the start. The odor of methylamine was detectable throughout the reaction, and the rate of evolution appeared to decrease near the end. Attempts to make coatings of the product on aluminum led to brittle, flaky films that did not encourage further effort.

4. Reaction of methylphenyldichlorosilane with aniline

To determine whether an aniline derivative of methylphenyldichlorosilane might polymerize better than a methylamine or ammonia derivative, methylphenyldichlorosilane, 95.5 g (0.50 mole), was dissolved in 30 ml of benzene and added dropwise to 464.6 g (5.0 moles) of aniline in 250 ml of benzene. The solution was refluxed for 4 hours, and the precipitate was removed by filtration. The benzene and excess aniline were distilled off at reduced pressure, and a viscous, red-brown liquid, 125.1 g (82% of theory), was obtained as the product. After standing for 3 days at room temperature, it was partially crystalline.

A portion of the crude product was heated in air in a Teflon beaker at 185°C for 3 days. About two-thirds of it evaporated, but the remainder was a smooth, homogeneous, resilient, fairly tough black polymer. Samples of the black polymer and of Viton A were heated in air at 425°C. The Viton A became hard in 15 minutes, but the methylphenyl derivative still retained some resilience after an hour. The crude product of the reaction between aniline and methylphenyldichlorosilane was distilled at 190-195°C at 0.04 mm pressure. The pale yellow distillate crystallized and melted at 72-80°C. Two recrystallizations from Skellysolve B raised the melting point to 77-80°C, and two additional recrystallizations did not change it. The elemental composition was:

Found: Carbon, 72.98%; hydrogen, 6.76%; nitrogen, 8.47%; silicon, 10.2%; total, 98.41%.

Calculated for dianilinomethylphenylsilane, $C_{19}H_{20}N_2Si$: Carbon, 74.95%; hydrogen, 6.62%; nitrogen, 9.20%; silicon, 9.23%.

NMR spectra indicated that the ratio of methyl : NH : phenyl groups was 1 : 2 : 3, which agrees with theory. However, identification is not claimed because of the departure from the theoretical elemental analysis. Therefore, it is called methylphenyl anilino silazane.

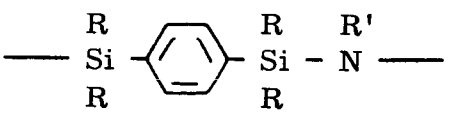
A sample of crude methylphenyl anilino silazane, 5.0 g (0.018 mole), and aluminum ethoxide, 0.19 g (0.0012 mole), were heated at 190-195°C for 3 hours. The pressure was reduced by an aspirator, and an undetermined amount of volatile liquid was removed. Heating was continued at 220-230°C for 5 hours, and the pressure was reduced again to strip off the volatiles. The product was a brittle solid at room temperature. Attempts to make coatings of it or to decrease its brittleness by further polymerizations were unsuccessful. The main discussion of aluminum ethoxide reactions is in Section XII.

V. POLYMERS MADE FROM PHENYLENE-BRIDGED SILYLAMINES

A. Discussion

Work on silicon-nitrogen polymers with phenylene groups in the main chain was undertaken because the chlorosilanes involved had structures that were expected to favor the formation of linear polymers instead of cyclic compounds. The polymers were expected to have good thermal stability because of the large amount of aromaticity in the chain. This expectation was justified, and tough, flexible polymers of this type with good thermal stability have been made. One of them was elastic at temperatures above 100°C and retained its elasticity for 30 minutes or more at 400°C. Another had promising properties as a coating agent. Only a relatively small portion of the appropriate investigation of these polymers has been completed. The initial work on these polymers was described in the preceding annual report,[13] and the work during the past year is described here.

Polymers were prepared from 1,4-bis(dimethylchlorosilyl)-benzene and from 1,4-bis(diphenylchlorosilyl)benzene by treating them first with methylamine or ammonia and subsequently polymerizing the derivatives by heating. The derivatives that have been made are represented by the following formula:



R = methyl or phenyl

R' = methyl (from methylamine)
or
hydrogen (from ammonia)

The polymers made from materials in which R was phenyl and R' was either methyl or hydrogen were invariably hard and brittle. They seem relatively less promising, because of brittleness, than the polymers made from materials in which R was methyl and R' was either hydrogen or methyl.

A tough red-brown elastomer was made from the compound in which both R and R' were methyl. The elastomer was made by heating the compound in air for 24 hours at 250°C, and it was still elastic after 30 minutes at 400°C. It lost its elasticity on standing at room temperature but regained it immediately on being heated to 100°C. The same uncured compound, in which R and R' were methyl, was used to impregnate glass cloth to form a flexible laminate that may be useful for gaskets. Four layers of glass cloth were superimposed, impregnated with the liquid, and cured 24 hours at 190°C and 1 hour at 250°C. The product was tan in color. It appeared to be between Viton A and Teflon in both compressibility and thermal stability. If it is used as a gasket material, it may be desirable to heat the gaskets to 100°C before placing them in position. Several subsequent preparations of the elastomer failed by a small degree to reproduce the initial toughness and thermal stability, but a later preparation did reproduce the desirable properties. The cured polymer dissolved slowly in tetrahydrofuran, and it was found to have a molecular weight of 110,000.

The material in which R was methyl and R' was hydrogen formed a fairly tough, white solid on being heated overnight at 250°C while nitrogen was bubbled through it. An additional 24 hours of heating under the same conditions failed to produce a significant further change. The product was applied to an aluminum panel from a benzene solution, and it cured to a tough, flexible, colorless coating on being heated 30 minutes at 350°C.

Both the ammonia and methylamine derivatives of 1,4-bis(dimethylchlorosilyl)benzene were exposed to gamma radiation. Neither was changed appreciably, except that they both darkened when they were exposed to 27.7 million roentgens. The methylamine derivative appeared to crystallize more slowly after it had been exposed to 13.4 million roentgens and heated to 300°C for an hour. For comparison Teflon and Viton A were irradiated also. Teflon became brittle after exposure to 9 million roentgens. Viton A lost its cohesion at the surface after being exposed to 13.4 million roentgens and being held at 300°C for an hour, but the main mass was intact and flexible even after exposure to 27 million roentgens.

Liquid prepolymers made with methylamine (R and R' = methyl) were also exposed to 27 million roentgens of gamma radiation. They became slightly more viscous, and they solidified on being heated at 250°C for 45 minutes, whereas the unirradiated liquids required 16 hours of heating before they became solid at this temperature. The solids produced after irradiation appeared to be slightly stronger, but a precise comparison of strengths was not made.

B. Experimental Details

1. Reactions with 1,4-bis(dimethylchlorosilyl)benzene

a. Preparation of 1,4-bis(dimethylchlorosilyl)benzene

The method of Sveda[14] was used to prepare 1,4-bis(dimethylchlorosilyl)benzene in a 5-liter, 3-neck flask fitted with a stirrer, and an extraction device. The extraction device consisted of a still with a partial take-off head which was arranged to return the distilled solvent to the reaction flask through a reservoir of p-dibromobenzene. In the flask were placed 62.0 g (2.54 moles) of magnesium turnings, 350 ml of dry diethyl ether, and 328 g (2.54 moles) of dimethyldichlorosilane. The system was swept with dry nitrogen, and the reaction was started by adding 8 g of methyl iodide. The flask was warmed slightly to reflux the ether which extracted the p-dibromobenzene (200 g, 0.848 mole) from the reservoir. As the dibromobenzene returned to the flask, the exothermic reaction kept the ether distilling. After the reaction was complete (2 hours), the mixture was refluxed for 2 hours. The mixture was filtered under anhydrous conditions, the cake was washed with ether, and the ether solutions were combined and distilled. The distillation was interrupted twice to remove the magnesium salts by filtration. When most of the ether was gone, 400 ml of dry toluene was added to insure removal of the dichlorosilane by further distillation at atmospheric pressure. The product remaining in the flask was then distilled twice at reduced pressure, and the fractions obtained were:

1. 3.0 g, 92-110°C at 1.5 mm pressure, dark red liquid
2. 90.0 g, 110-132°C at 1.5 mm pressure, pink crystals
3. 3.0 g, 132-182°C at 1.5 mm pressure, pink crystals
4. 4.0 g, residue, dark red crystals

Fraction 2 had a neutral equivalent of 145 (theory, 131.7), and it melted at 80-87°C. Sveda[14] reported a melting point of 87°C.

A second preparation of 1,4-bis(dimethylchlorosilyl)benzene yielded a fraction with b.p. 98°C at 0.4 mm. This fraction had a neutral equivalent of 150 (theory, 131.7). The neutral equivalent was determined by weighing a small sample into a glass-stoppered vial, opening the vial under alcohol, and titrating with standard alkali. This fraction was further purified in a Fisher Zone Refiner, Model 341 A. After 12 cycles, the product had a neutral equivalent of 137.

b. Reaction of 1,4-bis(dimethylchlorosilyl)benzene with methylamine and polymerization of the product

The first reaction of 1,4-bis(dimethylchlorosilyl)benzene, Fraction 2 (above), with methylamine was carried out as follows: In a 300-ml, 3-neck flask fitted with a thermometer, stirrer, reflux condenser, and gas-inlet tube were placed 18.6 g (0.071 mole) of 1,4-bis(dimethylchlorosilyl)benzene and 225 ml of dry benzene. The solution was stirred under an atmosphere of methylamine for 2 hours, and then refluxed for 1 hour. The Beilstein Test for halogens was negative. The solid was filtered off, and the benzene was removed by distillation. The yellow, viscous, liquid product weighed 15.3 g. The molecular weight was 715 (average of 700 and 730). This and similar materials are subsequently referred to as the "methylamino prepolymer."

The yellow, viscous liquid was polymerized in a mold made by milling a depression in a Teflon block. The liquid, about 2 mm deep in the mold, was placed in an oven in air at 250°C. Over a period of 24 hours it first formed a scum, then it solidified to an elastic red-brown solid. When cool, it could be stretched to about 3 times its length without breaking. In an hour at room temperature, it became more rigid and tough, so that it could not be stretched by hand, but it could still be bent double without breaking. Reheating at 250°C for a few seconds restored the elasticity. This polymer was designated 3205-55-4. It retained some resilience after being held at 400°C for 30 minutes. Attempts to cure the liquid prepolymer in glass vessels were less satisfactory, because the product adhered to the glass.

The elastic red-brown solid was soluble in tetrahydrofuran. It was found by light scattering to have a molecular weight of 110,000.

Attempts to polymerize the methylamino prepolymer by heating it in nitrogen were unsuccessful; the material remained liquid.

Subsequent repetitions of the reaction of 1,4-bis(dimethylchlorosilyl)benzene with methylamine led to prepolymers with lower viscosities. An example is a reaction that was started with a sample of Fraction 2 that was purified in the zone refiner as described above. The purified 1,4-bis-(dimethylchlorosilyl)benzene was treated with methylamine by the method above, and the pale yellow oily liquid product obtained was poured into a Teflon mold to a depth of about 2 mm and cured at 250°C for 16 hours. The resulting solid was wrinkled, and it could be torn easily. It was initially elastic, but it crystallized and became flexible but inelastic in about 3 hours at room temperature. After it was held at 400°C for 15 minutes and then cooled, it was considerably weaker. The more intense efforts to purify the silicon halide starting material had not resulted in improvements.

Later it was found that precuring at lower temperatures followed by a period at 250°C reproduced the original toughness, elasticity, and stiffness of Polymer 3205-55-4 reasonably well. One such sample, Polymer 3205-105-3 was sent to Marshall Space Flight Center where it was examined for elongation and tensile strength. To prepare this sample the liquid methylamino prepolymer was cured in air at 200°C for 120 hours and at 250°C for 24 hours. At room temperature on an Instron machine with a crosshead speed of 0.05 inch per minute, the elongation at break was 300%. The tensile strength of the original sample was 1000 psi and of the drawn sample was 4000 psi. A similar polymer, 3205-105-4, that was cured at 190°C for 4 hours and at 250°C for 24 hours contained 0.9% nitrogen which was 14% of the original amount.

Attempts to polymerize the methylamino prepolymer by heating it at 200°C under reduced pressure caused a decided increase in viscosity. Attempts to cure the resulting material at 250°C for 24 hours did not reproduce the desired toughness of sample 3205-55-4. There was some evidence that the curing rate of the sample heated under reduced pressure was slightly faster than that of the untreated prepolymer, but the improvement was not of practical significance.

Because the purification of 1, 4-bis(dimethylchlorosilyl)benzene seemed to have an undesirable effect, a sample of the compound was treated with a small amount of water before reaction with methylamine. 1, 4-Bis(dimethylchlorosilyl)benzene, 9. 0 g (0. 03 mole), was dissolved in benzene, 200 ml, and 0. 05 g (0. 003 mole) of water was added. After stirring for 1 hour at room temperature, small droplets remained visible in the mixture. When the temperature was raised to 80°C, the droplets disappeared in 5 minutes. Methylamine was then added in excess. After the benzene was distilled off, the clear, yellow, viscous product weighed 7. 0 g. It was less viscous and less cloudy than products made similarly but without the water.

The methylamino product made with water formed a highly elastic, slightly tacky solid when heated at 250°C for 48 hours. When left at room temperature for an hour, it crystallized and was tough and flexible but not elastic. A sample, 3205-129-3, was examined for tensile strength and elongation at Marshall Space Flight Center. It had 100% elongation at break and a tensile strength of 840 psi for the original sample and 2600 psi for the drawn sample.

A sample of the methylamino prepolymer was heated in a 43-ml stainless steel bomb in air at 190°C for 40 hours. The product was a viscous, clear, brown liquid. Further heating in air resulted in formation of a brittle solid. With oxygen in the bomb a friable, brown, waxy solid was produced.

Another sample of the methylamino prepolymer was heated with air bubbling through it for 16 hours at 250°C. It polymerized to a dark yellow, viscous liquid that was then used as a vehicle for a pigmented coating. The polymer, 1 part, was dissolved in benzene, 9 parts; and the solution was mixed with aluminum powder, 0. 1 part. The suspension was spread evenly on a stainless-steel panel, and the benzene was allowed to evaporate. The panel was heated at 400°C for 30 minutes and at 600°C for 30 minutes. The coating remained in place, and it could not be scratched with a fingernail. After the panel was bent over a mandrel with a radius of 4 mm, the coating could be scratched where it had been bent. The coating was not an electrical insulator, so apparently, the organic part of the vehicle was still present only in a small amount, if at all.

The methylamino prepolymer was used to impregnate four superimposed layers of glass cloth in a shallow Teflon mold. The impregnated cloth was then heated at 190°C for 24 hours. The mat was turned over several times during the first 8 hours of the curing period. At the end of 24 hours, the mat was tacky at room temperature. Heating for 1 hour at 250°C eliminated the tackiness. Heating at 450°C for 15 minutes caused some cracking on the surface, but the polymer did not lose its toughness, and the mass remained intact.

Thick solid samples of a tough elastomer were made by stirring the methylamino prepolymer periodically as it was being cured. The prepolymer in a layer 10 mm deep was heated in a Teflon mold at 250°C and stirred every 30 minutes. It gradually became thicker, and stirring was discontinued after 4-5 hours when it became apparent that the viscosity was too high for the material to coalesce if stirred again. Subsequent heating at 190°C for 20 hours and at 250°C for 60 hours completed the cures. The products were soft, rubbery, brown polymers. They crystallized, as usual, on standing at room temperature and became rubbery again when heated above 100°C.

Experiments to study the effects of radiation were done with gamma radiation from cobalt-60 at a rate of 1.4×10^5 roentgens per hour. The liquid methylamino prepolymer appeared to polymerize faster after exposure to 27 million roentgens; they became solid in 45 minutes at 250°C, whereas 16 hours would have been required without irradiation. A sample of the solid polymer (3205-55-4) exposed to 13.4 million roentgens appeared unchanged, except that it was slightly darker. After being heated at 300°C for an hour, it remained elastic for 8 hours at room temperature, whereas the original polymer crystallized in an hour. After exposure to the same dose of radiation, Teflon became brittle, and Viton A appeared to be unchanged, but the latter could be scratched on the surface after it was heated at 300°C for an hour. Further exposure to a total of 27 million roentgens of gamma radiation produced no further changes in any of the three compounds.

c. Reaction of 1,4-bis(dimethylchlorosilyl)benzene with ammonia and polymerization of the product

Rochow[15] mentioned having prepared an elastomeric polymer with good stability at 400°C by treating 1,4-bis(dimethylchlorosilyl)benzene with ammonia. He did not recount any attempts to evaluate it for practical utility.

In this laboratory, the reaction with ammonia was run as follows: In a 300-ml, 3-neck flask fitted with a thermometer, stirrer, reflux condenser, and gas-inlet tube were placed 23.5 g (0.089 mole) of Fraction 2 (Section V.B. 1.a., above) and 150 ml of benzene. The solution was stirred in an atmosphere of ammonia for 3 hours and then allowed to stand overnight. The Beilstein Test for halogens in the supernatant liquid was negative, so the solid was filtered off, and the benzene was removed by distillation. The white, waxy solid product weighed 14.0 g (76% of theory, based on the repeating unit). The molecular weight as determined by Galbraith Laboratories, Inc., by vapor osmometry was 3375 (average of 3350 and 3400).

A sample of the white, waxy solid product was heated at 250°C for 24 hours in air. The product formed was a thick cream-colored grease at room temperature. Further heating for a few minutes at 400°C in air converted it to a soft, tacky, resilient solid.

Another sample of the white, waxy solid was placed in a Teflon beaker and heated overnight at 250°C in a nitrogen atmosphere. The product was a thin liquid at 250°C and a viscous, stringy liquid at room temperature. A portion became brittle and cracked when heated at 450-500°C on an aluminum panel.

Another sample of the white, waxy, solid polymer was placed in a 10-mm Pyrex test tube and heated at 250°C while nitrogen was bubbled slowly through the melt for 18 hours. The cooled product was an opaque, white, tough solid that softened at 185-190°C. This solid was heated in a layer about 1 mm deep in a Teflon mold at 350°C for 2 hours in air. The product was a transparent, rubbery film at 250°C. At room temperature it was a transparent, brown, flexible solid that could be torn easily.

Another sample of the white, waxy solid polymer was placed in a 50-ml Erlenmeyer flask with a long neck. The polymer melted on being heated to 250°C, and nitrogen was bubbled through the melt for 64 hours. The product was still a clear, colorless liquid at 250°C, and it became a white solid on cooling to room temperature. The white solid was applied to an aluminum panel as a 10% solution in benzene and cured for 30 minutes at 350°C. The film was tough and flexible, and it could not be scratched with a fingernail or a 9H pencil.

Another sample of the white, waxy solid polymer was dissolved in benzene to form a 10% solution; 1% by weight of aluminum powder was stirred into the solution, and the mixture was applied to aluminum panels in thin layers. These did not cure to solid films in 16 hours at 250°C, nor in 1 hour at 300°C, 350°C, or 400°C. Similar results were obtained with the white, waxy, solid polymer produced by heating in nitrogen as described in the preceding paragraph.

2. Reactions of 1,4-bis(diphenylchlorosilyl)benzene

Reactions of 1,4-bis(diphenylchlorosilyl)benzene with ammonia and methylamine suggested that the products would be harder and more brittle than their methyl-substituted counterparts as described in Section V.B.1.

a. Preparation of 1,4-bis(diphenylchlorosilyl)benzene

The first attempt to prepare 1,4-bis(diphenylchlorosilyl)benzene was by a method taken from the work of Newing, Davis, and Towers.[16] In a 3-liter, 3-neck flask fitted with a stirrer, reflux condenser, thermometer, and dropping funnel were placed 29.2 g (1.2 mole) of magnesium turnings and 300 ml of tetrahydrofuran. To this was added dropwise, 141 g (0.6 mole) of p-dibromobenzene that had been dissolved in tetrahydrofuran.

The resulting mixture was refluxed 2 hours and then left over the weekend under a nitrogen atmosphere. The solution of the Grignard Reagent was added over a period of 2 hours to 303 g (1.2 mole) of diphenyldichlorosilane in 500 ml of tetrahydrofuran. The mixture was stirred for 3 hours and left under a nitrogen atmosphere overnight. The tetrahydrofuran was removed by rapid distillation, and the residue was stirred with 1800 ml of heptane. The liquid suspension was filtered while all of the apparatus was in a polyethylene bag filled with nitrogen. The colorless filtrate was cooled in dry ice and then left overnight in a refrigerator, whereupon a few crystals formed. These were filtered off in a nitrogen atmosphere and were found to have a neutral equivalent of 504 (theory, 256). Three successive recrystallizations reduced the neutral equivalent to 384. The product weighed 10.7 g (3.5% yield).

A more successful preparation of 1,4-bis(diphenylchlorosilyl)benzene was accomplished by the method that Sveda[14] used to make the methyl compound in a 5-liter, 3-neck flask fitted with a stirrer and an extraction device. The extraction device consisted of a still with a partial take-off head that condensed the distillate and delivered it to a reservoir of p-dibromobenzene. After it trickled through the dibromobenzene, the distillate was returned to the reaction flask. The distilling-extraction cycle could be run continuously, and the rate of extraction could be controlled by adjusting the boiling rate and a stopcock in the partial-take-off still head.

In the reaction vessel were placed 62.0 g (2.54 moles) of magnesium turnings, 500 ml of dry diethyl ether, and 643 g (2.54 moles) of diphenyldichlorosilane. The system was swept with dry nitrogen, and the reaction was started by adding 8 g of methyl iodide. The flask was warmed slightly to reflux the ether which extracted the p-dibromobenzene (200.0 g, 0.85 mole) from the reservoir. As the dibromobenzene returned to the flask, the exothermic reaction kept the ether distilling. When the extraction of the p-dibromobenzene was complete, the reaction subsided; and the mixture was refluxed for 2 hours. The mixture was filtered inside a polyethylene bag filled with dry nitrogen, the cake was washed with ether, and the ether solutions were combined and distilled. The distillation was interrupted three times to remove the magnesium salts by filtration. When most of the ether was gone, 500 ml of n-heptane was added to precipitate the 1,4-bis(diphenylchlorosilyl)benzene. The total product was 24 g of a tan, crystalline material.

The neutral equivalent of the product was 269 (theory, 255.8).

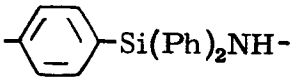
b. Reaction of 1,4-bis(diphenylchlorosilyl)benzene with ammonia and polymerization of the product

The reaction of the sample of 1,4-bis(diphenylchlorosilyl)benzene with a neutral equivalent of 269 (from the second preparation above) with ammonia was run as follows: In a 300-ml, 3-neck flask fitted with thermometer, magnetic stirrer, reflux condenser, and gas-inlet tube were placed 200 ml of dry benzene and 12 g (0.023 mole) of 1,4-bis-(diphenylchlorosilyl)benzene. The solution was stirred in an atmosphere of ammonia for 2 hours and then refluxed for 1 hour. The solution was allowed to stand overnight. The Beilstein Test for halogens in the clear, supernatant liquid was negative, so the solid was filtered off, and the benzene was removed by distillation. The product (9.7 g) was a creamy, waxy solid. The molecular weight was 590 (average of 580 and 600).

The creamy, waxy solid was heated in air at 250°C for 24 hours. At 250°C it was a viscous, brown, soft solid that could be drawn into long, brittle fibers. At room temperature it was hard and brittle.

The crystalline product with a neutral equivalent of 384 from the first preparation above, presumably crude 1,4-bis(diphenylchlorosilyl)-benzene, was treated with ammonia in the following manner: In a 1-liter, 3-neck flask fitted with stirrer, reflux condenser, thermometer, and gas-inlet tube were placed 200 ml of benzene and 10.7 g (0.0209 mole) of crude 1,4-bis(diphenylchlorosilyl)benzene. Ammonia was passed through the gas-inlet tube for 9 hours, and a positive pressure of ammonia was maintained on the reaction with the aid of a balloon on top of the condenser. The Beilstein Test for halogens was negative. The solution was refluxed for 3 hours. After being cooled, the reaction mixture was filtered to remove ammonium chloride. The benzene was distilled off; and the residue, 7.2 g, was a creamy, waxy solid. The elemental composition was:

Found: Carbon, 73.61%; hydrogen, 5.34%; nitrogen, 2.39%; silicon, 11.5%; remainder, 7.16%.

Calculated for  : Carbon, 79.07%; hydrogen, 5.53%; nitrogen, 3.07%; silicon, 12.33%.

c. Reaction of 1,4-bis(diphenylchlorosilyl)benzene with methylamine and polymerization of the product

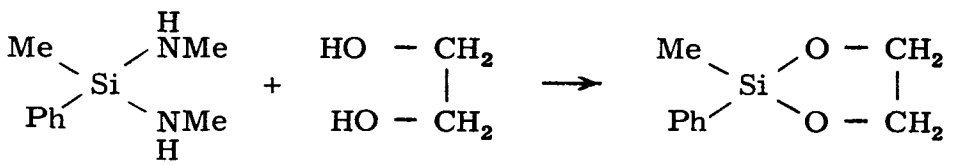
The reaction with methylamine was run as follows: In a 300-ml, 3-neck flask fitted with thermometer, magnetic stirrer, reflux condenser, and gas-inlet tube were placed 12.0 g (0.023 mole) of 1,4-bis(diphenylchlorosilyl)benzene. Methylamine was passed over the stirred contents of the flask for 2 hours. The reaction mixture was refluxed for 1 hour and allowed to stand overnight. The Beilstein Test for halogens in the supernatant liquid was negative, so the solid was filtered off, and the benzene was removed by distillation. The product, 11.0 g, was a tan, waxy solid; molecular weight, 560 (average of 550 and 570). Behavior on polymerization of this compound was almost identical with that of the compound described in Section V.B.2.b. above. After being heated in air at 250°C for 24 hours, it was a viscous, brown, soft solid that could be drawn into long, brittle fibers. At room temperature it was hard and brittle.

VI. REACTION OF DIAMINOSILANES WITH POLYFUNCTIONAL HYDROXY AND AMINO COMPOUNDS

A. Discussion

It has been shown at the George C. Marshall Space Flight Center that diaminosilanes react with dihydroxybenzenes to form tough polymers with excellent thermal stability. Similar reactions have been tried here with diaminomethylphenyl silazanes. It was postulated that the methyl group attached to the silicon would enhance the flexibility of the polymers. In addition, attempts have been made to bring about the corresponding reaction of diaminosilanes with diaminobenzenes instead of dihydroxybenzenes.

The product called methylphenyl methylamino silazane was produced in the reaction of methylphenyldichlorosilane with methylamine (without triethylamine) as described in Section IV. B. 3. c. It reacted rapidly with hydroquinone, resorcinol, p,p'-biphenol, ethylene glycol, glycerol, phloroglucinol, and pentaerythritol. With hydroquinone, a black, tough, flexible, elastic polymer was obtained that remained flexible after heating 1 hour at 350°C. With resorcinol, a rigid polymer was formed. The incorporation of ethylenediamine silazane produced a resilient polymer that remained resilient for 30 minutes at 400°C. With biphenol, a tough, rigid polymer was formed that was soft enough at 300°C to be molded or stretched, and it had interesting properties as an adhesive. With phloroglucinol (1, 3, 5-trihydroxybenzene), a rubbery material was produced that became rigid and brittle in 10 minutes at 125°C. With ethylene glycol, a viscous liquid was formed that did not distill at 120°C at 0.04 mm pressure. When heated on an aluminum panel, the product formed a film that protected the metal from acid even after the panel was bent. Cyclization probably occurred to a large extent with the ethylene glycol, but no pure product was isolated.



With glycerol, a solid polymer was formed that was soft at 50°C. Long fibers could be pulled from the melt, but the low softening point of the polymer made it of relatively little interest. With pentaerythritol, a yellow, sticky solid was produced. Heating this solid at 190°C produced a fairly tough, resilient solid that became very brittle in 30 minutes at 400°C.

Benzidine (4, 4'-diaminobiphenyl) and p-phenylene diamine reacted slowly with methylphenyl methylamino silazane; the products were hard and brittle. Evidently, the molecular weights were too low for the polymers to be useful.

Methylphenyl anilino silazane was made by the reaction of methylphenyldichlorosilane with aniline (Section IV. B. 4). The product was probably crude dianilinomethylphenylsilane. It reacted slowly with benzidine, and the product was a soft solid at room temperature. Attempts to cure the product further by heating in thin films caused much of it to evaporate. Apparently, polymerization occurred too slowly for any useful products to be formed. The reaction of methylphenyl anilino silazane with p, p'-biphenol produced a polymer that softened at about 110°C.

Hexaphenylcyclotrisilazane and ethylene glycol reacted readily at 175-225°C to produce a soft elastic polymer with excellent elongation but low tensile strength and slow recovery time. It broke readily when the rate of elongation was rapid, but it could be stretched to a thin film if pulled slowly. The elastomer was soluble in benzene, and it had moderately good stability as a coating. After being heated on an aluminum panel at 400°C for 17 hours or 500°C for 1 hour, the coating formed from the elastomer protected the aluminum from hydrochloric acid except where the panel had been bent. However, the polymers and coatings were sensitive to moisture on prolonged exposure.

The reaction of hexaphenylcyclotrisilazane with ethylene glycol and a small amount of glycerol produced a tougher elastomer, but it still did not have outstanding thermal or hydrolytic stability in comparison with other new polymers that have been made in this program.

B. Experimental Details

1. Reactions of the methylphenyl methylamino silazane

The preparation of the methylphenyl methylamino silazane, which was probably largely bis(methylamino)methylphenylsilane, was described in Section IV. B. 3. c.

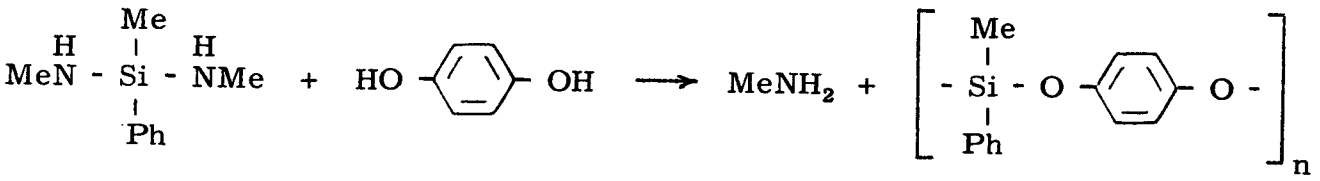
a. With hydroxybenzenes

(1) Hydroquinone

The crude methylphenyl methylamino silazane, 8.9 g [0.05 mole, if the compound was bis(methylamino)methylphenylsilane] was mixed with 6.6 g (0.06 mole) of hydroquinone, and a rapid reaction occurred. The crude material was known to be impure; probably cyclic compounds were present. Hence, a slight excess of hydroquinone above the stoichiometric amount was used. The mass was stirred at 260-270°C for 4 hours. The film formed on heating a small part of the resulting liquid on a panel was brittle and had poor adhesion. The liquid polymerized further in 2 hours at 300-310°C, and then brittle fibers could be pulled from the melt as it cooled to a hard solid.

The crude methylphenyl methylamino silazane was distilled as described in Section IV. B. 3. c., and Fraction 2 appeared to be the purest fraction, but it still contained some cyclic compound.

A portion of Fraction 2, 8.9 g, was dissolved in 20 ml of tetrahydrofuran, and 6.6 g (0.06 mole) of hydroquinone in 40 ml of tetrahydrofuran was added dropwise with stirring. Methylamine was evolved. The solution was refluxed for 4 hours, then the solvent was distilled off at reduced pressure to leave 13.9 g (102% of theory) of a viscous red-orange liquid. The expected reaction was:



The red-orange liquid product was heated for 18 hours at 190°C in air in a Teflon beaker. The product was a small black disc, 5-mm thick and 20 mm in diameter. It was tough, pliable, and elastic. It became fairly rigid on standing for several hours, but pliability returned when it was flexed. A small strip of it was still flexible after being heated in air at 350°C for an hour. In another experiment, heating at 190°C for 48 hours converted the red-orange liquid to a harder and less tough polymer that cracked when it was strongly flexed. The inclusion of ethylenediamine silazane, 10%, in another sample, improved the flexibility but decreased the strength.

In an effort to increase the molecular weight, the hydroquinone was recrystallized, and another reaction with the methylphenyl methylamino silazane was run as described above. Again a viscous, red-orange liquid was obtained; but this product was not successfully cured in 18 hours at 190°C. Instead it became a viscous, black mass. Heating for a total of 42 hours at 190°C produced a flexible, black polymer that broke on repeated flexing.

Another reaction was tried in triethylamine instead of tetrahydrofuran. The initial product was a sticky, pink solid rather than a red-orange liquid. After 3 days in air at 190°C, it became a brown, viscous liquid. Heating overnight in air at 190°C converted it to a brittle, foamed solid that had no apparent properties of interest.

(2) Phloroglucinol

In a 50-ml, 3-neck flask equipped with a reflux condenser, thermometer, dropping funnel, and magnetic stirrer were placed 2.5 g (0.02 mole) of anhydrous phloroglucinol and 20 ml of tetrahydrofuran. The solution was stirred, and 5.4 g (0.03 mole) of methylphenyl methylamino silazane in 15 ml of tetrahydrofuran was added. When the addition was complete, the reaction mass was a soft, rubbery material that was not soluble in tetrahydrofuran, benzene, or acetone. The rubbery material, after being heated at 125°C for 10 minutes, became brittle. Further heating at 400°C for 2 minutes caused the polymer to become black and friable.

(3) Mixtures of hydroquinone and phloroglucinol

aa. 100:1 mole ratio, hydroquinone to phloroglucinol

In a 100-ml, 3-neck flask equipped with reflux condenser, thermometer, dropping funnel, and magnetic stirrer were placed 3.3 g (0.03 mole) of recrystallized hydroquinone, 0.037 g (0.0003 mole) of anhydrous phloroglucinol, and 30 ml of tetrahydrofuran. To this solution was added 5.4 g (0.03 mole) of methylphenyl methylamino silazane dissolved in 20 ml of tetrahydrofuran. The solution was refluxed 5 hours. The solvent was distilled leaving 4.9 g of a yellow, viscous polymer. At this point the effect of the phloroglucinol was not apparent.

A 9:1 mixture of the yellow, viscous polymer and ethylenediamine-silazane formed a semi-solid rubbery material on heating 97 hours at 190°C. Additional heating at 350°C caused the polymer to become friable with no resilience. If phloroglucinol had not been present, the polymer would have been resilient, according to previous experience.

Attempts to make coatings were unsuccessful because of brittleness and poor adhesion to aluminum.

bb. 10:1 mole ratio, hydroquinone to phloroglucinol

The method for the preparation of this compound was similar to that described in the preceding section. The procedure differed in that 0.026 mole of hydroquinone and 0.0026 mole of phloroglucinol were used with the 0.03 mole of methylphenyl methylamino silazane. The solvent was distilled from the reaction product, and 5.7 g of a cream-colored, sticky material was recovered.

A mixture of the cream-colored, sticky polymer and ethylenediamine silazane in a 9:1 ratio was warmed 2 minutes at 190°C, and then removed from the oven and stirred. As the mixture cooled, it became a rubbery solid that crumbled easily, and the product could not be remelted at 350°C. This material became brittle after being heated at 350°C for 2 hours. Because of its poor strength, it was less promising than other materials that have better thermal stability.

Coatings on aluminum panels cracked and flaked on being heated at 350°C for 18 hours.

(4) p, p'-Biphenol

The methylphenyl methylamino silazane was treated with p, p'-biphenol with and without tetrahydrofuran as a solvent. In a 25-ml, 3-neck flask, fitted with a magnetic stirrer, reflux condenser, and thermometer were placed 5.4 g (0.03 mole) of the methylphenyl methylamino silazane and 5.5 g (0.03 mole) of p, p'-biphenol (4, 4'-dihydroxybiphenyl). A vigorous reaction occurred with foaming. The resulting viscous mass was heated at 235-270°C for 3.5 hours. When the product was hot, it was sticky and rubbery; when cool, it was hard and tough. The mass contained air and was not homogeneous, so an attempt was made to fuse it by heating 30 minutes at 350°C and 10 minutes at 400°C in a Teflon beaker. It did not fuse, but it did become tougher. The small disc, 8-mm thick and 20 mm in diameter could not be broken with the fingers; and vigorous pounding with a hard rubber mallet did not break it. A portion of the disc was dissolved in acetone, and the resulting solution was used to make a coating on aluminum. After 1 hour of heating at 185°C, the coating appeared to be intact, but it could be peeled off with the knife blade. The freed film was transparent, flexible, and fairly strong. A sample heated at 370°C for 16 hours became brittle.

In another preparation, the methylphenyl methylamino silazane, 5.4 g (0.03 mole) in 20 ml of tetrahydrofuran was dropped into 5.5 g (0.03 mole) of p, p'-biphenol in 50 ml of tetrahydrofuran. Some amine was evolved, and the temperature rose 15°C. The solution was refluxed for 4 hours, then the solvent was distilled off, and the residue was heated at 270°C for 1.5 hours. The product was a sticky, tan solid that became hard and brittle on standing. When heated on an aluminum panel in an attempt to form a coating it flaked badly.

Recrystallized p, p'-biphenol was used in another reaction without solvent as described above. A vigorous reaction occurred, and the mass was then heated at 250°C for 3 hours and at 290°C for 1 hour. At 290°C, the product was very viscous and somewhat elastic. Fibers could be pulled from the melt. Small discs about the size of a dime were made by fusing portions of the polymer on an aluminum panel, and these discs were so tough that they could barely be broken with the fingers.

The reaction in solvent appeared preferable, and so another was run to obtain additional material. In a 100-ml, 3-neck flask equipped with dropping funnel, reflux condenser, thermometer, and magnetic stirrer were placed 3.4 g of methylphenyl methylamino silazane [0.0187 mole if the compound had been pure bis(methylamino)methylphenylsilane] and 20 ml of tetrahydrofuran. To this 3.5 g (0.0187 mole) of recrystallized p,p'-biphenol dissolved in 30 ml of tetrahydrofuran was added through the dropping funnel. The mixture was refluxed for 2 hours, and the solvent was distilled. The reaction temperature was raised to 250°C for 2 hours and then to 290°C for 1 hour. The product was a viscous, tan liquid at 290°C, and it was rigid and tough at room temperature. When placed in boiling water it became flexible and elastic with slow recovery time. By light scattering in tetrahydrofuran, it was found to have a molecular weight of 150,000. A piece of the polymer and of Viton A were heated at 425°C. After 15 minutes, the experimental polymer had swelled and split open, and it was friable when pressed with a spatula. The Viton A had cracked on the surface, but it retained a small amount of resilience.

The polymer with a molecular weight of 150,000 was heated at 300°C for 4 hours, and then a small piece was dissolved in tetrahydrofuran to form a gel. The gel was spread on the end of a 0.25-inch wide aluminum strip, and then another strip was clamped to it to form a lap joint with an overlap of 0.067 sq in. The joint was heated at 300°C for 30 minutes. The joined strips were subjected to a shear test, and the joint broke at 300 pounds. Thus the shear strength was 4800 psi. On stainless steel strips, the value was 4600 psi.

A small piece of the polymer (molecular weight 150,000) was heated at 300°C for 2 hours and then pressed between Teflon sheets in a compression mold at 800 psi and 135°C. A sheet 2-mils thick was formed; it was flexible but broke when creased sharply.

(5) Resorcinol

The reaction with resorcinol was tried to provide a comparison of the meta substituted compound with the para substituted hydroquinone. In a 100-ml, 3-neck flask equipped with magnetic stirrer, reflux condenser, thermometer, and dropping funnel were placed 6.6 g (0.06 mole) of recrystallized resorcinol and 20 ml of tetrahydrofuran. To this was added 10.8 g (0.06 mole) of methylphenyl methylamino silazane in 20 ml of tetrahydrofuran. The solution was refluxed for 5 hours; then the solvent was distilled off leaving 12.7 g of a viscous liquid.

A small amount of the viscous liquid was heated in a 5-ml Teflon beaker at 190°C for 90 hours to form a tacky solid disc. Heating the disc at 400°C for 0.5 hour caused it to become hard on the surface. An additional 0.5 hour at 400°C caused the disc to become friable.

The viscous liquid was mixed with ethylenediamine silazane in a 9:1 ratio and heated in a Teflon beaker for 23 hours at 190°C to form a tacky rubbery disc about 2 mm thick. After 30 minutes at 400°C it was still flexible. Another 30 minutes at 400°C made it rigid. It was easily broken with the fingers.

b. With polyalcohols

(1) Ethylene glycol

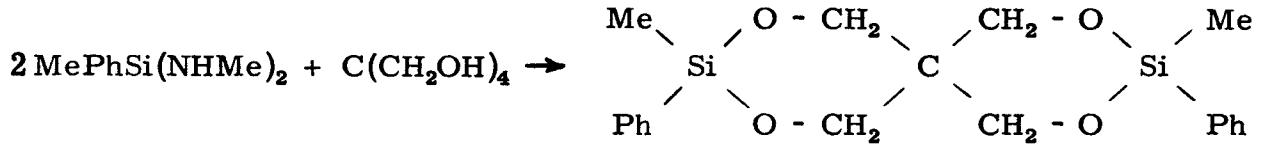
Ethylene glycol, 1.26 g (0.03 mole, freshly distilled), was placed in a 25-ml, 3-neck flask fitted with a reflux condenser, thermometer, and magnetic stirrer; and methylphenyl methylamino silazane, 5.4 g (0.03 mole, Fraction 2, Section IV. B. 3. c.) was added with stirring. A vigorous reaction ensued, and the temperature rose 19°C. The temperature was raised to 170-175°C for 3 hours while stirring was continued. Then the temperature was raised to 250-255°C for 3 hours. The product was a mobile, yellow, liquid at 255°C. An attempt to distill yielded no volatile material even when the pot reached 120°C and the pressure was 0.04 mm. The liquid product, when spread on aluminum and heated at 190°C for 18 hours, 350°C for 1 hour, and 400°C for 2 hours, formed a thin, transparent colorless film that did not crack when bent and that protected the panel from 19% hydrochloric acid. Evidently some polymeric material was present in the liquid product to form the coating.

(2) Glycerol

Glycerol, 1.8 g (0.02 mole, freshly distilled), and methylphenyl methylamino silazane, 5.4 g (0.03 mole, Fraction 2, Section IV.B.3.c) were stirred at 230°C for 5 hours. The melt was viscous throughout the entire period. Long fibers could be pulled from the melt, but they had low tensile strength. On being cooled, the melt solidified at about 50°C to form a transparent, tan, tacky product that softened on exposure to the atmosphere. When the product was applied to aluminum and cured as a coating, it adhered poorly and could be scraped off easily.

(3) Pentaerythritol

The reaction with pentaerythritol was tried with the thought that a highly cross-linked material might be formed with the characteristics of a potting compound. However, cyclization was also possible according to this reaction.



In a 50-ml, 3-neck flask equipped with dropping funnel, reflux condenser, thermometer, and magnetic stirrer were placed 3.4 g (0.025 mole) of pentaerythritol and 20 ml of tetrahydrofuran. To this was added 9.0 g (0.05 mole) of methylphenyl methylamino silazane. The solution was refluxed for 5 hours; then the solvent was distilled off leaving 7.2 g of a yellow, sticky liquid.

A small amount of the yellow, sticky liquid was placed in a 5-ml Teflon beaker and heated 138 hours at 190°C. The product was a resilient polymer, but it became very friable after being heated at 400°C for 1 hour.

Attempts to form coatings on aluminum produced brittle films with poor adhesion.

c. With diamines

(1) Benzidine

Recrystallized benzidine, 5.5 g (0.03 mole), and methylphenyl methylamino silazane, 5.4 g (0.03 mole), were mixed in 40 ml of tetrahydrofuran and refluxed for 20 hours. There was no evidence of reaction such as darkening or an increase in viscosity. The amount of methylamine evolved was almost negligible.

The same quantities of the two materials were then mixed without solvent. On heating, methylamine was first evolved at 60°C; the mixture became viscous when it reached 130°C; and continued heating at 230°C for 3.5 hours was accompanied by darkening and a slow increase in viscosity. The product solidified to a dark brown, brittle solid when it was cooled. Attempts to form coatings on aluminum produced shiny, jet-black, brittle films with poor adhesion.

(2) Phenylenediamine

Attempts to produce polymers from p-phenylenediamine and the methylphenyl methylamino silazane gave results similar to those just described.

2. Reactions of the methylphenyl anilino silazane

a. With p, p'-biphenol

The methylphenyl anilino silazane was prepared by the reaction of methylphenyldichlorosilane with aniline as described in Section IV. B. 4. The reaction product was distilled and recrystallized as described, and NMR spectra showed the final product to be mainly dianilinomethylphenylsilane.

The recrystallized material, 4.75 g (0.0156 mole), was placed in a 50 ml, 3-neck flask equipped with a distilling head, thermometer, and magnetic stirrer. Recrystallized p, p'-biphenol, 2.9 g (0.0156 mole), was added, and the mixture was warmed slowly to 230°C and held at that temperature for 2 hours. The pressure was reduced with a water aspirator, and 2.0 g of a clear liquid distilled. As the product in the reaction flask cooled, fibers could be pulled from the melt. The softening temperature was about 110°C, but at room temperature the fibers were flexible enough to permit tying knots. When exposed to 9 million roentgens of gamma radiation, the fibers became brittle.

Attempts to form coatings on aluminum produced smooth brittle films with poor adhesion.

b. With benzidine

Equimolar quantities of benzidine and the methylphenyl anilino silazane were mixed in tetrahydrofuran and refluxed for 11 hours with no visible signs of reaction. The solvent was removed, and the reactants were heated at 205-210°C for 2 hours. A small amount of liquid, believed to be aniline, distilled at 175°C. The residue was a dark, sticky solid. Attempts to polymerize the solid further by heating it on a panel or in an open beaker at 185°C for 16 hours resulted largely in evaporation. The reaction was evidently too slow to be useful.

3. Reactions of hexaphenylcyclotrisilazane

Hexaphenylcyclotrisilazane was shown at Marshall Space Flight Center to form polymers when heated with difunctional hydroxyaromatic compounds. This investigation of the reaction with ethylene glycol was undertaken as an extension of the previous work. Triethylamine was tried in the reaction as a promoter of polymerization, but it had no beneficial effect. Instability of the products on prolonged standing in air was a disadvantage,

a. With ethylene glycol and triethylamine

In a 50-ml, 3-neck round-bottom flask, equipped with a magnetic stirrer, thermometer, dropping funnel, and reflux condenser were placed 5.0 g (0.0084 mole) of hexaphenylcyclotrisilazane and 20.0 g (27.8 ml, 0.198 mole) of purified triethylamine. Then 1.39 ml (1.56 g, 0.0252 mole) of recently distilled ethylene glycol in 7.2 g (10.0 ml, 0.071 mole) of triethylamine was dropped with stirring into the reaction flask. When no rise in temperature occurred, heat was applied and the mixture was stirred at 50-60°C for 1.0 hour. The heat input was then increased, and the mixture was refluxed at 90°C for 1.0 hour. At the end of this time, the hexaphenylcyclotrisilazane had not gone into solution and did not appear to have reacted. The triethylamine was distilled off, and a viscous, tan liquid remained. This residue was stirred at 105-108°C for 4.0 hours. The temperature was then increased to 290°C, and, in 0.5 hour, the mixture became very viscous. The product was 5.92 g of tan, tacky material with some elastic properties.

A small amount of the tan, tacky polymer in a 10-ml Teflon beaker placed in an oven at 175°C for 3.25 hours was converted to a tacky solid which cooled to a malleable disc that could be stretched to about four times its diameter without breaking, provided it was not stretched suddenly. The disc was returned to an oven at 300°C for 15 minutes. While at 300°C, it was a dark brown liquid; after cooling, it was an elastic solid which could be stretched to a transparent film without tearing. The stretched film returned to its original shape slowly. This elastomer was brittle at the temperature of dry ice.

Another disc was formed by heating the tan, tacky polymer in a Teflon beaker for 2.0 hr at 175°C. The product was a clear, yellow-orange solid, that was tacky at 175°C but, when cooled, was a non-tacky elastic solid. A 10% solution of this product in benzene was dried on an aluminum panel and the panel was heated then at 125°C for 1.5 hr and at 400°C for 5.0 hr. A smooth coating formed that was unaffected by 19% hydrochloric acid even after being bent. A similar coating heated at 500°C for 1.0 hr was smooth and unaffected by 19% hydrochloric acid except where the panel was bent. Another coating heated at 400°C for 18 hr also was clear and unaffected by acid except where it was bent. Coatings prepared at room temperature, 125°C, and 175°C were not adequately cured.

An attempt was made to cross-link the tan, tacky polymer with benzoyl peroxide. The polymer, 0.6 g, was placed in a 10-ml Teflon beaker, and 0.07 g of benzoyl peroxide was added. The mixture was heated at 125°C for 1.5 hr and at 175°C for 5.5 hr. At 175°C, the product was a dark brown liquid; on cooling, it formed a solid that could be pulled into a film. After being heated further at 125°C for 16 hr, the polymer was still fluid; on recooling, it was elastomeric. A small piece about 2 in. long was pulled slowly into a thin 2.5-foot strip without breaking.

b. With ethylene glycol and without triethylamine

In a 100-ml, 3-neck, round-bottom flask equipped with a magnetic stirrer, reflux condenser, thermometer, and dropping funnel were placed 15.0 g (0.0252 mole) of hexaphenylcyclotrisilazane and 4.17 ml (4.68 g, 0.0756 mole) of ethylene glycol. Heat was applied, and in 0.75 hr the temperature reached 225°C, the reactants formed a homogeneous melt, and a strong odor of ammonia was detected. The mixture was stirred at 185-195°C for 1.5 hr. Then the temperature was increased gradually, and after 1.5 hr the melt was very viscous at 320°C. On being cooled, the product was clear, tan, tacky, and elastic; it weighed 17.98 g. The elemental composition was:

Found: Carbon, 68.50%; hydrogen, 5.89%; nitrogen, less than 1%

Calculated for $[-Si(Ph)_2-OCH_2CH_2O]_n$: Carbon, 69.38%; hydrogen, 5.82%; oxygen, 13.21%; silicon, 11.59%.

A small amount of this tacky, elastic product exposed to 23 million roentgens of gamma radiation became even stickier. Another sample of this product that had been heated at 175°C until it became solid (about 4 hours) appeared to be unaffected by exposure to 10 million roentgens of gamma radiation.

c. With ethylene glycol in 5% excess

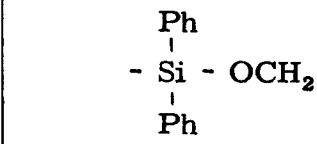
In a 25-ml, 3-neck, round-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser were placed 5.0 g (0.0084 mole) of hexaphenylcyclotrisilazane, and 1.46 ml (1.64 g, 0.0265 mole) of recently distilled ethylene glycol. Heat was applied, and a homogeneous melt was formed when the temperature reached 220°C (about 35 minutes). After a total of 2.75 hours of heating, during which time the temperature rose gradually to 300°C, the product became too viscous to be stirred with a magnetic stirrer. On cooling the product formed a tan, transparent, tacky material, similar to the product obtained from equivalent amounts of hexaphenylcyclotrisilazane and ethylene glycol. The product weighed 5.54 g. This represents a 91% yield, if the product is assumed to be

$$\left(-\overset{\overset{Ph}{|}}{\underset{\underset{Ph}{|}}{Si}}-OCH_2-CH_2O-\right).$$

A small amount of the tan material was placed in a 10-ml Teflon beaker and heated at 175°C for 2 hours. The polymer was soft but did not flow at this temperature. On cooling, it formed a non-tacky, flexible material that was fairly tough, but could be pulled apart easily with the fingers. On further heating for a total of 17.5 hr at 175°C, the sample became softer. When cool, the polymer was less tough than it was initially. It was still soluble in benzene. Coatings on aluminum panels prepared from 10% benzene solutions of the samples heated for 2 hr and for 17.5 hr were unaffected by 19% hydrochloric acid on the flat surfaces after being heated at 400°C for 18 hr. However, the coatings did not protect the aluminum where the panels were bent.

d. With ethylene glycol and 5% excess hexaphenylcyclotrisilazane

In a 25-ml, 3-neck, round-bottom flask equipped with a magnetic stirrer, reflux condenser, and thermometer were placed 1.39 ml (1.56 g, 0.0252 mole) of ethylene glycol and 5.25 g (0.0088 mole) of hexaphenylcyclotrisilazane. Heat was applied, and a homogeneous melt was obtained when the temperature reached 190°C (about 50 minutes). The temperature was increased until it reached 260°C after 1.25 hour of heating. The mixture did not increase in viscosity in 2.5 hours at this temperature. The temperature was then increased to 360°C for 2 hours. Again there was no apparent increase in viscosity even though the product became darker in color. The temperature was increased to 386°C for 0.75 hour. The mixture was then a dark brown liquid that refluxed at this temperature, and the odor of escaping ammonia was detected. As the product cooled, it solidified to a dark brown, elastic, tacky solid at 150°C. This product weighed 6.10 g. The theoretical yield was 6.11 g, based on



as the formula.

A small amount of the brown, elastic solid was heated at 175°C for 5 hours in air in an effort to reduce the tackiness. It remained liquid at 175°C. On cooling, it formed a non-tacky, flexible material that could be stretched to a transparent film about twice the size of the original. On further heating for 63.5 hours at 175°C, the sample became more elastic but less tough. If pulled slowly a 1-inch sample could be stretched about 2 feet.

Coatings were prepared on aluminum from a 10% benzene solution of the elastomer that had been heated for 68.5 hours. After being heated at 400°C for 18 hours, the panels were bent and immersed in 19% hydrochloric acid. Except for a few pinholes, the aluminum was unaffected by the acid in the coated areas. Further experimentation revealed that weight retention in such coatings was only 10-15%. They degenerated on standing in air for a month.

e. With ethylene glycol and 5% glycerol

In a 25-ml, 3-neck, round-bottom flask equipped with a thermometer and reflux condenser were placed 5.0 g (0.0084 mole) of hexaphenylcyclotrisilazane, 1.39 ml (1.56 g, 0.0252 mole) of ethylene glycol, and 0.10 ml (0.12 g, 0.0013 mole) of recently distilled glycerol. Heat was applied, and in 20 minutes, when the temperature reached 180°C, the melt became homogeneous. The viscosity increased noticeably as the temperature rose. The melt became too viscous for stirring in 1.25 hour when the temperature reached 332°C. When cool, the product was 5.98 g of a transparent, tan, tacky solid. A small amount of this material heated in a 10-ml Teflon beaker at 175°C for 2 hours remained soft and tacky; and it cooled to an elastic disc which was tougher than those formed from the other reactions of hexaphenylcyclotrisilazane with ethylene glycol. The polymer's thermal stability was appraised by heating a small piece of the disc at 400°C. After being heated 10 minutes and then cooled, the sample was brittle in the thinner places; after heating 20 minutes, the whole sample crumbled on cooling. Another portion of the disc heated at 350°C for 30 minutes remained liquid while hot and was still flexible when cool, but it had little strength. After 45 minutes at 350°C, the sample crumbled on cooling. However, the polymers made from hexaphenylcyclotrisilazane and ethylene glycol became tacky on standing in air, and so they are of relatively little interest.

Coatings were made by dissolving the tan, tacky solid to form a 10% solution in benzene and spreading the solution on aluminum. After being heated at 400°C for 18 hours, the panel was bent and immersed in 19% hydrochloric acid. The coating remained intact, except where it was bent, but it disintegrated on standing for several weeks.

VII. ALKALI METAL DERIVATIVES OF CYCLIC SILAZANES AS INTERMEDIATES FOR SYNTHESIS

A. Discussion

1. General summary

The N-alkali metal derivatives of silylamines react with compounds having active halogens, thereby offering a method of preparing a variety of substituted silylamines.

$$\equiv SiNH \xrightarrow{K} \equiv SiNK \xrightarrow{R\text{-}X} \equiv SiN\text{-}R$$

The reaction has been studied extensively in this and other laboratories in attempts to make polymers and liquids of exceptional thermal stability. It now appears that the reaction is subject to disproportionation, which makes it difficult to obtain pure products except by extensive fractional crystallization. Disproportionation also interferes with the formation of linear polymers.

In the present work the seven routes represented in Figure 1 have been explored. Five of these could have led to polymers, and the other two could have led to polymers or materials that might have been useful as lubricants or hydraulic oils.

The attachment of benzyl, methyl, and trimethylsilyl groups to silazanes increased their hydrolytic stability. The resulting compounds were polymerized by heating (Polymer 1, Figure 1) but no polymers of high molecular weight were obtained. The polymerization reaction was studied in detail in the hope that a better understanding of it would lead to a method of getting higher molecular weights and better strength, but a practical route to better polymers was not found.

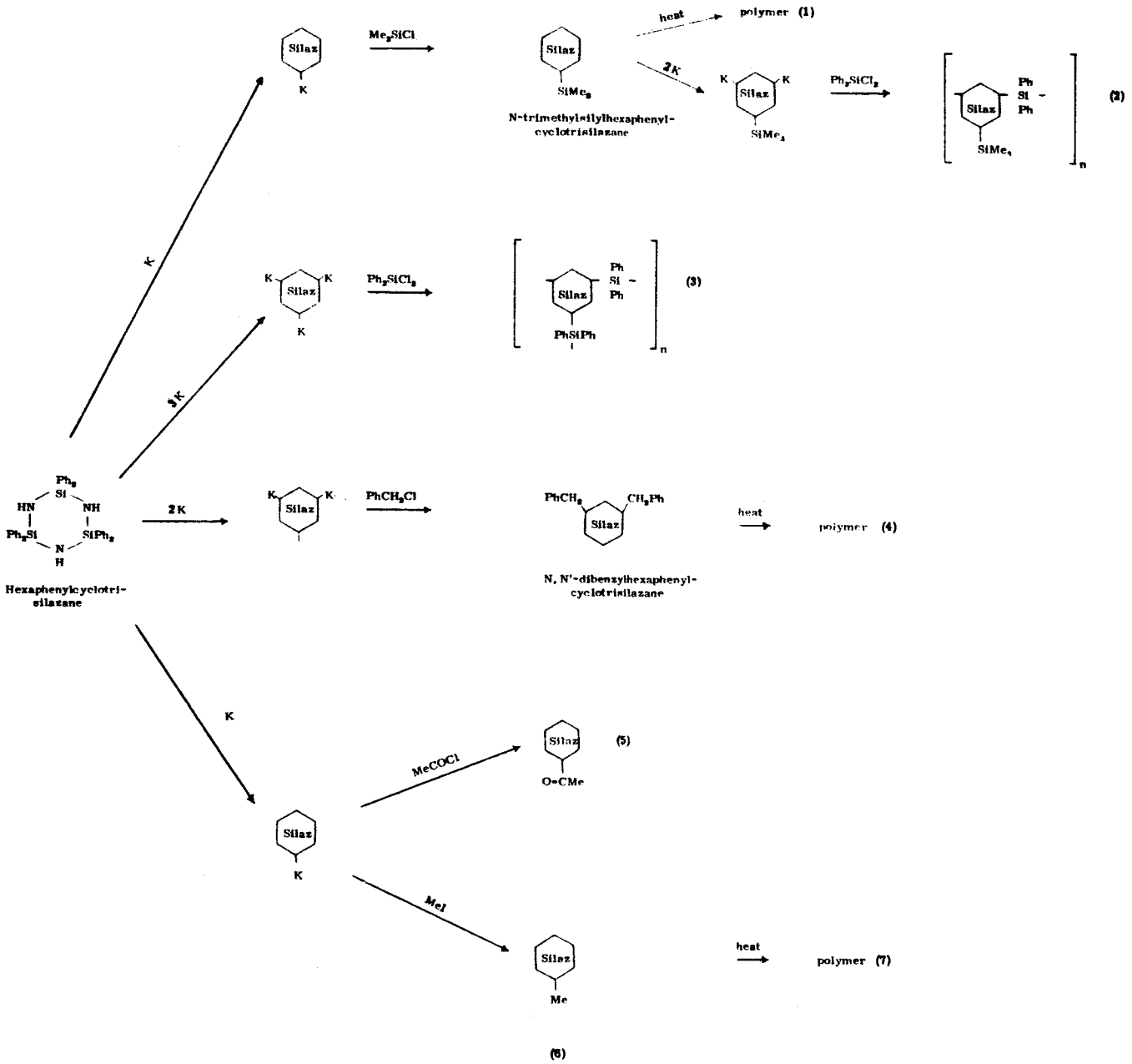


Figure 1. Routes of Reaction for N-Potassium Silazanes.

The reaction to produce Polymer (2) of Figure 1, reaction of the dipotassium derivative of N-trimethylsilylhexaphenylcyclotrisilazane with diphenyldichlorosilane, could produce a high molecular weight linear polymer if it proceeded as shown. The product obtained was a cloudy orange-colored grease, and the expected potassium chloride by-product was not successfully isolated. Consequently, the grease was dissolved in benzene and treated with dry ammonia. The precipitate that formed was filtered off, the solvent was removed from the filtrate, and a tan resin was obtained. Attempts to polymerize the resin by heating at 400-425°C produced a black material that could not be poured at that temperature and that was a brittle, benzene-soluble solid at room temperature. It did not appear to be promising as a coating.

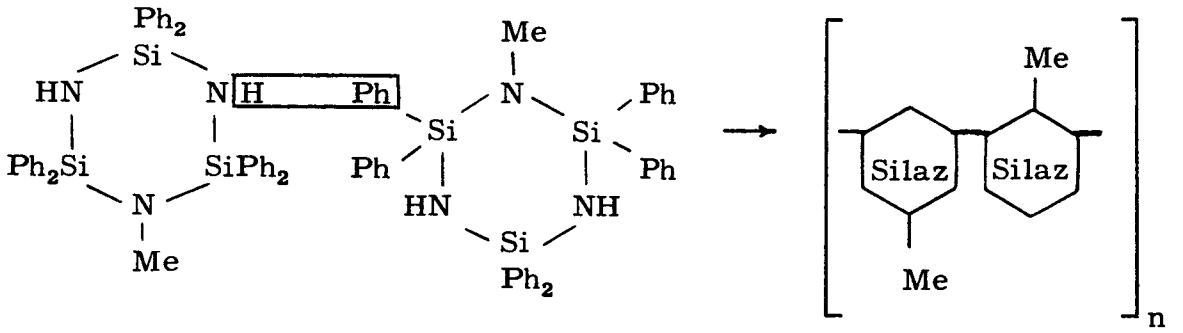
An attempt was also made to reduce the functionality further by introducing two trimethylsilyl groups into the hexaphenylcyclotrisilazane molecule. However, attempts to polymerize the N, N'-bis(trimethylsilyl)-hexaphenylcyclotrisilazane by heating produced only brittle solids.

Experience with Polymer (3) was similar to that with Polymer (2). It was formed by treatment of the tripotassium derivative of hexaphenylcyclotrisilazane with diphenyldichlorosilane. Linear polymerization was not likely since the original hexaphenylcyclotrisilazane was trifunctional in the reaction. The molecular weight of the product was evidently not high, because the resin was relatively soft and soluble in benzene.

N, N'-Dibenzylhexaphenylcyclotrisilazane polymerized in 30 hours at 380°C to a solid at that temperature (Polymer 4). The polymer was soluble in benzene. It was brittle, and it appeared to have no special merit as a coating.

An attempt to prepare an acetyl derivative of hexaphenylcyclotrisilazane (Product 5) by treating the mono-potassium derivative with acetyl chloride was not successful. More than half of the hexaphenylcyclotrisilazane was recovered, and the remainder of the product was a soft, tan resin. The acetyl derivative evidently was not formed, or it was unstable and decomposed to form a polymer of undetermined character.

The reaction of the N-potassium derivative of hexaphenylcyclotrisilazane with methyl iodide produced a crystalline compound (Product 6), but it was not successfully separated from the starting material and other methylated products. Attempts to polymerize it by heating produced a black, foamed polymer with no properties that appear to be promising. The desired reaction was this:



Similar attempts to produce N-octadecyl and N-decyl derivatives were also unsuccessful.

2. Studies of the polymerization of N-trimethylsilylhexaphenylcyclotrisilazane

N-trimethylsilylhexaphenylcyclotrisilazane condensed on heating above 450°C to form, first, a high-melting benzene-soluble polymer and, then, an infusible and insoluble polymer.

It was evident from the data obtained that the mechanism of polymerization had much in common with that of the polymerization of hexaphenylcyclotrisilazane and proceeded by the elimination of benzene through the interaction of ≡ Si - Ph and H - N = groups in adjacent molecules.

The polymerization was conducted in a glass vessel over a gas burner, and samples were taken periodically for analysis. The polymerization was also conducted in a distilling apparatus, and the volatile products were trapped for analysis. The results did not permit any simple interpretation of the mechanism. The samples that were taken periodically during polymerization indicated that a steady state was reached at approximately the composition $C_{6.5}H_{5.5}N_{0.5}Si_{1.0}$. The data are listed in Table III and plotted graphically in Figure 2. However, the data cannot be considered conclusive, because the analyses failed to add up to 100%, and it does not appear likely that the missing amounts can be attributed entirely to oxygen. The similarity of Figure 2 to a comparable curve drawn for hexaphenylcyclotrisilazane[17] is striking. Condensation occurred rapidly while the mass was being heated from 480-560°C, and then it changed only a little during another 50 minutes of heating at 550°C.

The volatile products of the condensation polymerization were 80% benzene, as shown by gas chromatography. About 10% consisted of four compounds boiling lower than benzene, including hydrogen and methane, and the other 10% consisted of 13 compounds boiling higher than benzene. Toluene, xylene, and biphenyl were believed to be present in the condensate, but they were not completely identified.

It is clear that the polymerization of N-trimethylsilylhexaphenylcyclotrisilazane is more complicated than that of hexaphenylcyclotrisilazane. There seems little merit in carrying the identification of products further. The most important question is whether a useful polymer can be made by thermal polymerization, and it is evident that the trimethylsilyl group has not decreased the functionality of the molecule significantly. So far, the polymers have been excessively brittle, but they do have high softening points and high thermal stability, and they are soluble in benzene. Higher molecular weight is needed.

Table III. Characteristics of Precursors of the N-trimethylsilylhexaphenylcyclotrisilazane Polymer

	Starting material	I	II	III	IV	V
Time of heating, min	0	6	10	12	15	65
Temperature when sample taken, °C	-	481	540	558	-	550
Approximate melting point of sample, °C	168-170	61-70	128-142	above 350	infusible	infusible
Physical state, when cool	crystalline	vitreous	vitreous	vitreous	foamed, vitreous	foamed, vitreous
Solubility in benzene	soluble	soluble	soluble	slightly soluble	insoluble	insoluble

	Starting material		I		II		III		IV		V	
	Composition, %	Combining ratio[a]	Composition, %	Combining ratio[a]	Composition, %	Combining ratio[a]	Composition, %	Combining ratio[a]	Composition, %	Combining ratio[a]	Composition, %	Combining ratio[a]
Carbon	70.87	5.90	69.54	5.77	69.06	5.74	65.69	5.46	62.85	5.24	57.79	4.81
Hydrogen	5.97	5.93	5.54	5.50	5.62	5.58	4.50	4.46	4.67	4.64	4.17	4.14
Nitrogen	6.65	0.48	6.51	0.46	7.10	0.51	6.27	0.44	4.06	0.29	5.56	0.39
Silicon	16.6	0.59	18.41[b]	0.65	17.5	0.62	19.6	0.69	21.1	0.75	21.3	0.76
	100.09				99.28		96.06		92.68		88.82	

Ratios to Si = 4: Theoretical formula, $C_{39}H_{41}N_3Si_4$

Carbon	40.0	35.5	37.0	31.7	28.0	25.3
Hydrogen	40.2	33.8	36.0	25.9	24.8	21.8
Nitrogen	3.26	2.83	3.29	2.55	1.55	2.05

[a] Combining ratio = $\frac{\text{composition}}{\text{atomic weight}}$

[b] Too little sample for silicon analysis, silicon by difference.

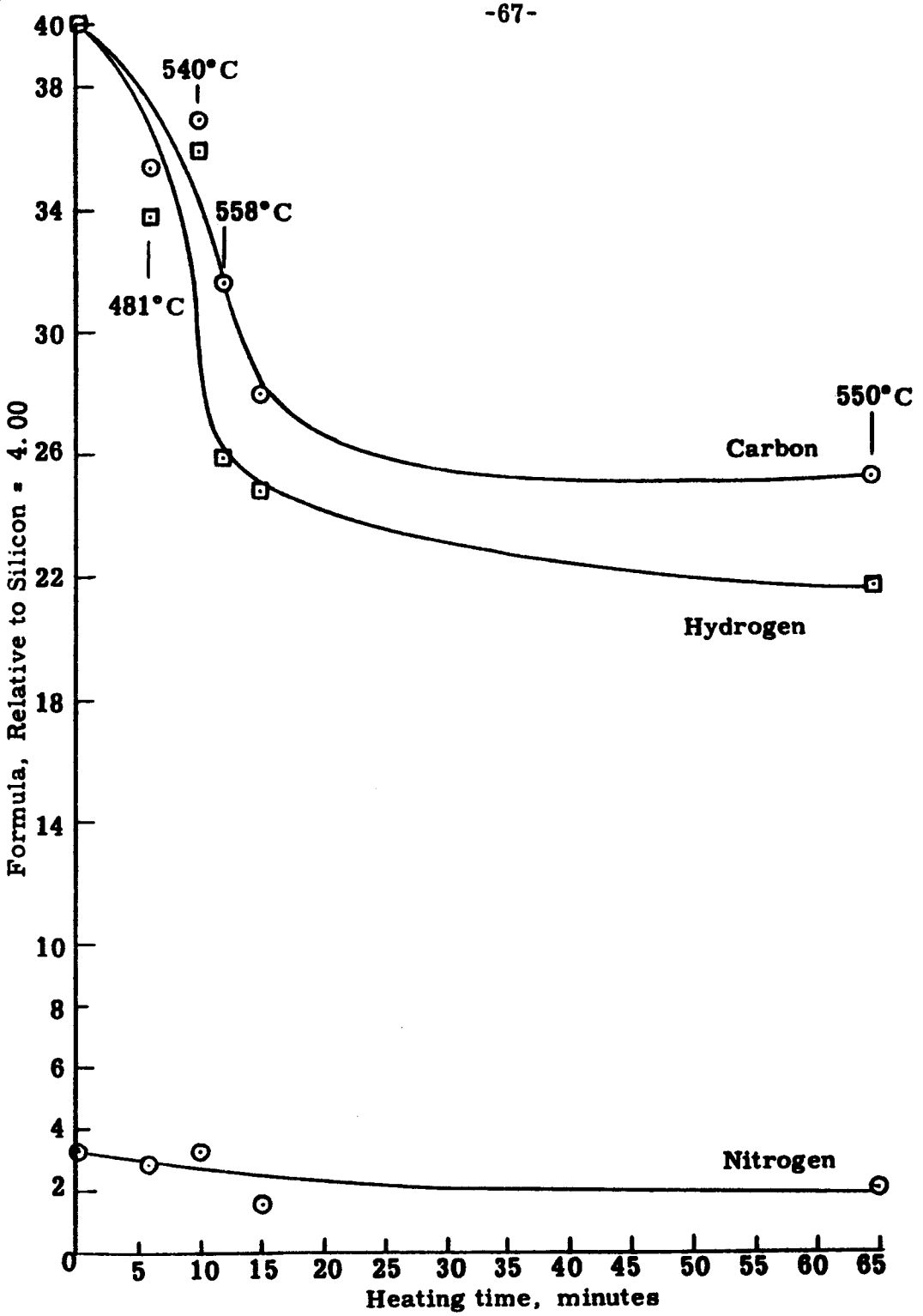


Figure 2. Change in Composition During Thermal Polymerization of N-Trimethylsilylhexaphenylcyclotrisilazane (See Table I)

B. Experimental Details

1. Polymerization of trimethylsilyl derivatives of hexaphenylcyclotrisilazane

a. Exploratory polymerization

(1) Polymerization of N-trimethylsilylhexaphenylcyclotrisilazane

N-trimethylsilylhexaphenylcyclotrisilazane was prepared as described in the preceding annual report[18] by treating hexaphenylcyclotrisilazane with potassium and trimethylchlorosilane. N-Trimethylsilylhexaphenylcyclotrisilazane (0.5013 g, 0.755 millimole) was placed in a test tube that was swept with nitrogen, and the tube was capped with crimped aluminum foil. The tube was then inserted through a hole in the door of an oven at 400°C with the capped end protruding from the oven. The compound melted immediately. After 8 hours, it was a dark brown liquid; and after 23 hours it was a dark brown solid. The solid did not crack on being cooled. It weighed 0.3610 g. It did not melt or foam when heated over a Meker burner on a spatula that became bright red. However, when the spatula was heated with a blast lamp, the polymer melted, smoked, and then burned. The elemental composition was:

Found: Carbon, 65.62%; hydrogen, 4.35%; nitrogen, 0.9%; silicon, 21.0%; total, 91.87%

Theory for N-trimethylsilylhexaphenylcyclotrisilazane: Carbon, 70.53%; hydrogen, 6.22%; nitrogen, 6.33%; silicon, 16.92%.

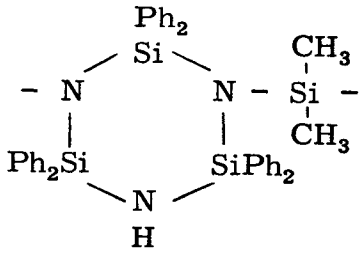
Nuclear magnetic resonance spectra showed that the ratio of the phenyl : trimethylsilyl : NH groups was 24 : 1 : 3.75 (theory for the starting material, 6 : 1 : 2). The low nitrogen analysis is, therefore, questionable.

A second sample of N-trimethylsilylhexaphenylcyclotrisilazane (0.5262 g, 0.795 millimole) became solid after being heated at 450°C for 5 hours. It was a dark brown solid that weighed 0.3398 g and that behaved much like the sample obtained at 400°C. The elemental composition was:

Found: Carbon, 62.96%; hydrogen, 4.63%; nitrogen, 5.75% silicon, 23.0%; total, 96.34%.

Nuclear magnetic resonance spectra showed that the ratio of the phenyl : trimethylsilyl : NH groups was 28 : 1 : 9. The methyl groups had undergone no apparent change, and so those present were there as trimethylsilyl.

It is difficult to draw a simple formula that fits the analytical data on the polymer. The increase in silicon content combined with the large increase in phenyl groups as indicated by NMR eliminates a simple repeating group such as the following:



Theory: Carbon, 70.43%; hydrogen, 5.75%; nitrogen, 6.48%; silicon, 17.34%

NMR: Ratio, phenyl : methyl : NH — 6 : 2 : 1

At 475°C, N-trimethylsilylhexaphenylcyclotrisilazane foamed partly and became solid in 4 hours. The entire mass was soluble in benzene. At 500°C a light tan foamed solid formed in 1.75 hours. It was not soluble in benzene.

Neither the 400° nor the 450°C polymer was visibly affected by concentrated hydrochloric acid or concentrated sulfuric acid in 2 hours at room temperature. After being in each of the acids for 18 hours, there was no visible effect, except a slight cloudiness that was visible on the surface of the 450°C polymer. Neither of the polymers was visibly affected by boiling in concentrated sulfuric acid for 10 minutes.

(2) Preparation and polymerization of N,N'-bis(trimethylsilyl)-hexaphenylcyclotrisilazane

aa. Preparation from N-trimethylsilylhexaphenylcyclotrisilazane

The procedure for preparation of N-trimethylsilylhexaphenylcyclotrisilazane used in this experiment is described in a previous report.[18]

In a 500-ml, 3-neck flask fitted with a magnetic stirrer, reflux condenser, thermometer, and dropping funnel were placed 60 ml of purified dioxane and 0.74 g (0.019 mole, 10% excess) of metallic potassium. Then 11.5 g (0.0173 mole) of N-trimethylsilylhexaphenylcyclotrisilazane dissolved in 100 ml of purified dioxane was added. The resulting solution was refluxed for 3 hours. At the end of this time, almost all the potassium had reacted. The solution was cooled, and 2.69 g (0.019 mole, 10% excess) of trimethylchlorosilane dissolved in 10 ml of purified dioxane was added over a 10-minute period. A white precipitate, presumably KCl, formed during the following 2 hours of refluxing. The reaction product was cooled and centrifuged. The precipitate, after being washed twice with dioxane, weighed 1.2 g (theory, 1.4 g).

The product was distilled to remove the dioxane, and the undistilled portion was dissolved in Skellysolve B.

Fractional recrystallization yielded 0.7 g (6.3% of theory) of crystalline product melting at 226-227°C. NMR spectra showed that the ratio of phenyl : trimethylsilyl : NH was 6 : 2 : 1 (theory, 6 : 2 : 1).

Found: Carbon, 68.98%; hydrogen, 6.51%; nitrogen, 5.78%; silicon, 19.1%

Calculated: Carbon, 68.51%; hydrogen, 6.71%; nitrogen, 5.71%; silicon, 19.07%.

The molecular weight by vapor osmometry was 724 (average 728 and 720); theory, 736.3. The determination was made by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Attempts to repeat this preparation were not successful. In one attempt, the procedure just described was followed as closely as possible, but with only 7.8 g of N-trimethylsilylhexaphenylcyclotrisilazane and equivalent amounts of the other reactants. The product consisted of 1.4 g of crystals, m.p. 161-164°C; 0.5 g of crystals, m.p. 167-168°C; and 5.8 g of a pale yellow grease. In another attempt, styrene was added in an attempt to achieve better reaction of potassium. The product consisted of five fractions as follows:

1. 0.8 g, m.p. 169-170°C
2. 0.1 g, m.p. 166-167°C
3. 0.6 g, m.p. 154-157°C
4. 1.3 g, m.p. 333-334°C
5. 8.0 g, pale yellow grease

NMR spectra revealed no disubstitution product in the grease.

bb. Additional attempts to prepare N,N'-bis(trimethylsilyl)-hexaphenylcyclotrisilazane

Additional attempts were made to prepare N,N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane both by monosilylation of N-trimethylsilylhexaphenylcyclotrisilazane and by bis-silylation of hexaphenylcyclotrisilazane in one step. In addition, a mixture that was believed to contain both mono and bis derivatives was treated with potassium and trimethylchlorosilane in an attempt to increase the amount of the bis derivative to the point where it could be isolated. Only the reaction just described that started with pure N-trimethylsilylhexaphenylcyclotrisilazane successfully produced the pure bis derivative, and in that reaction the yield was only 6.3%.

cc. Polymerization of N,N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane

N,N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane, 0.1011 g (0.14 millimole), was placed in an 8-mm test tube which was then swept with nitrogen. The open end was capped by crimping aluminum foil over the top, and the bottom was inserted into an oven through a hole in the door. The capped end was left outside of the oven. After 5 hours at 400°C, the material in the tube was a dark brown liquid, but it had become perceptibly more viscous. At the end of 13 hours at 400°C, the sample was solid. At the end of 23 hours at 400°C, no additional visible change had occurred. The solid, vitreous, brown product was not soluble in benzene; and it would not melt on a spatula at red heat. It was not foamed. In the 23 hours at 400°C, the sample lost 35% of its weight.

b. Studies of mechanism of polymerization of N-trimethylsilylhexaphenylcyclotrisilazane

(1) Samples taken periodically during polymerization

The procedure was taken from previous work on the polymerization of hexaphenylcyclotrisilazane.[19]

N-Trimethylsilylhexaphenylcyclotrisilazane, 3 g, was placed in a test tube. A 600°C thermometer was placed loosely in the test tube, and the apparatus was flushed with nitrogen. The test tube was heated gently with a gas flame, and the crystals melted at about 170°C. Continued heating produced a few bubbles, but the liquid did not appear to boil until the temperature reached 451°C. Boiling was continued while the melt temperature rose to 481°C in 6 minutes. At this time, heating was discontinued while Sample I was removed with a small stainless steel scoop. Heating was resumed, and after boiling for 4 additional minutes while the temperature rose to 540°C, Sample II was taken. After 2 additional minutes Sample III was taken at 558°C. As the scoop was withdrawn, brittle fibers formed. Solid began to appear in the tube shortly after Sample III was taken; and thereafter the temperature measurement was erratic because of poor contact between the walls of the tube, the reaction mixture, and the thermometer. Heating and stirring were continued until the entire mass solidified. The time of heating to complete solidification was 15 minutes. Sample V was obtained by heating the polymerized solid in an oven at 550°C for 50 minutes. The elemental analyses of the samples are given in Table III and are plotted in Figure 2.

(2) Identification of volatile products

The method used to trap the volatile compounds evolved when N-trimethylsilylhexaphenylcyclotrisilazane was polymerized was the same used in previous work on hexaphenylcyclotrisilazane.[20]

Approximately 1.8 g of N-trimethylsilylhexaphenylcyclotrisilazane was placed in the reaction vessel and weighed. The apparatus was assembled and swept with dry nitrogen. The nitrogen flow was stopped, the receiver was chilled, and the reaction vessel was heated gently with a burner to start condensation polymerization of the N-trimethylsilylhexaphenylcyclotrisilazane. The volatile material distilled and condensed throughout the system. When solidification became complete in the reaction vessel, heating was stopped. Each section of the apparatus was weighed after it reached room temperature. The starting material lost 0.5546 g or 31% of its weight. The volatile condensation product was analyzed by gas chromatography and found to be 80% benzene. Ten percent of the products were more volatile than benzene and consisted of four separate compounds including hydrogen and methane. Ten percent were less volatile than benzene. They consisted of 13 compounds and probably included toluene, xylene, and biphenyl, although these were not positively identified.

2. Polymerization of potassium derivatives of N-trimethylsilylhexaphenylcyclotrisilazane with diphenyldichlorosilane

The reactions leading to Polymer 2, Figure 1, were conducted as follows: In a 200-ml, 3-neck flask fitted with stirrer, reflux condenser, thermometer, and dropping funnel were placed 60 ml of purified dioxane and 1.09 g (0.0279 mole, 10% excess) of metallic potassium. Then 8.4 g (0.0126 mole) of N-trimethylsilylhexaphenylcyclotrisilazane dissolved in 100 ml of dioxane was added, and the solution was refluxed for 3 hours. At the end of this time, most of the potassium had reacted. The solution was cooled to 15°C and 3.5 g (0.0139 mole) of diphenyldichlorosilane was added. The viscosity of the solution increased immediately. The solution was refluxed for 2 hours.

Difficulty was encountered when attempts were made to separate the potassium chloride from the product. The dioxane was removed by distillation, and portions of the polymer were redissolved in benzene and Skellysolve, but potassium chloride did not separate. When it was heated on a panel, the polymer was converted to a white powder. The polymer was then dissolved in benzene, and ammonia was passed in for 1 hour. The solution was refluxed for 2 hours, cooled, and filtered. The benzene was distilled off leaving a cloudy tan resin in the pot as it cooled.

The resin melted when it was heated on a panel, and then it changed to a white powder. On heating a sample of the tan resin in the furnace at 400-425°C for 7 hours, it formed a black, brittle material that did not flow at 425°C but that melted when heated on a spatula below red heat. The black product was soluble in benzene. A coating formed by spreading a benzene solution on a panel and then heating over a flame cracked when the panel was bent. Another coating was formed by mixing the polymer with ethylenediamine in a 9:1 ratio and then curing for 15 minutes at 475°C. This coating was attacked by 19% hydrochloric acid and it could be scraped from the aluminum panel with a fingernail.

3. Polymerization of hexaphenylcyclotrisilazane with potassium and diphenyldichlorosilane

Polymer 3 of Figure 1 was produced as follows: In a 300-ml, 3-neck flask fitted with a magnetic stirrer, reflux condenser, thermometer, and dropping funnel were placed 60 ml of purified dioxane and 3.28 g (0.0838 mole, 10% excess) of metallic potassium. Then 15 g (0.0254 mole) of hexaphenylcyclotrisilazane dissolved in 120 ml of dioxane was added. The resulting solution was refluxed for 4 hours. At the end of this time, most of the potassium had reacted. The solution was cooled to 10°C, and 10.6 g (0.0419 mole) of diphenyldichlorosilane was added. The solution became thick immediately. The reaction was refluxed for 2 hours.

Difficulty was encountered in separating the potassium chloride from the product.

Approximately half of the sample was dissolved in Skellysolve "B" and centrifuged. The residue was extracted twice with benzene and centrifuged after each extraction. The residue at this time was a gel. The gel was dissolved in acetone and centrifuged leaving a white residue that appeared to be potassium chloride. The solvents were distilled to yield 10 g of an orange grease.

The remainder of the sample was dissolved in benzene and stirred in an atmosphere of ammonia for an hour. The solution was refluxed for 2 hours, cooled, and filtered. The benzene was distilled off, leaving 10.1 g of a thick, yellow-orange grease.

The grease last described above was heated at 300-325°C for 1 hour to form material that was a brown solid after cooling. A mixture of the brown solid with ethylenediamine silazane in a 9:1 ratio formed a product that had good adhesive properties when cured with glass or aluminum. Two aluminum panels were joined over an area of 1 square inch with the 9:1 mixture and heated at 400°C for 0.5 hour. After cooling, the shear strength of the joint was 200 pounds as measured on a Scott Tester. Another sample heated for 24 hours at 300-325°C had a shear strength of 172 pounds per square inch. Two other samples prepared from the first grease (9:1 ratio with ethylenediamine silazane) heated to 400°C for 3 hours separated at 160 pounds per square inch. A sample heated at 450°C for 1 hour had no strength.

Another reaction was conducted in a stainless steel bomb at higher temperature. In a 43-ml bomb was placed 20 ml of purified dioxane, 2.0 g (0.0034 mole) of hexaphenylcyclotrisilazane, and 0.4 g (0.0101 mole) of potassium. The bomb was closed and heated with shaking in an oven at 150°C for 4 hours. After being cooled, the bomb was opened, and no metallic potassium was seen. Then 1.28 g (0.0051 mole) of diphenyldichlorosilane in 10 ml of dioxane was added, and the bomb was heated with shaking at 150°C for 6 hours. The cooled product in solution was viscous, and there was some visible solid. The solution could not be filtered because of its viscosity. The product was diluted with Skellysolve "B" and centrifuged. The solid was then extracted repeatedly with acetone to separate the product into a soluble and an insoluble portion. The insoluble portion was potassium chloride. The soluble portions were evaporated, and the product was obtained as a brown resin, which decomposed when attempts were made to cure it on aluminum in the form of coatings. Evidently the use of higher temperatures in the polymerization was not beneficial.

4. Preparation and polymerization of N-benzyl derivatives of hexaphenylcyclotrisilazane

In a 500-ml, 3-neck flask fitted with a magnetic stirrer, reflux condenser, thermometer, and dropping funnel were placed 60 ml of purified dioxane and 1.09 g (0.0279 mole, 10% excess) of metallic potassium. The solution was heated until the potassium was well dispersed. Hexaphenylcyclotrisilazane, 15 g (0.0254 mole), dissolved in 120 ml of purified dioxane was added through the dropping funnel, and the resulting solution was refluxed for 3 hours. At the end of this time, all but a trace of the potassium had reacted. The solution was cooled, and 3.53 g (0.0279 mole) of benzyl chloride in 15 ml of dioxane was added. A white precipitate, presumably potassium chloride, formed during the following 6 hours of refluxing. The mixture was cooled, and the precipitate was filtered off. The residue, after being washed with dioxane and dried, weighed 1.8 g (theory for KCl, 2.08 g).

The dioxane was removed by distillation leaving an orange product that did not distill at a pot temperature of 145°C at 1.0 mm pressure. The product was dissolved in Skellysolve, and fractional crystallization yielded the following:

1. 2.4 g, m.p. 168-169°C
2. 0.6 g, m.p. 154-156°C
3. 7.3 g, m.p. 186-206°C
4. 5.0 g, viscous grease

15.3 g, total

NMR spectra of Fraction 1 indicated that it was N,N'-dibenzyl-hexaphenylcyclotrisilazane; the ratio of Si-phenyl to N-benzyl groups was 6:2 (theory for the N,N'-dibenzyl derivative, 6:2). The elemental composition of Fraction 1 was:

Found: Carbon, 77.22%; hydrogen, 6.03%; nitrogen, 5.46%; silicon, 10.4%

Calculated: Carbon, 77.77%; hydrogen, 5.87%; nitrogen, 5.44%; silicon, 10.92%

The yield was 15.7% of theory. The molecular weight was determined by Galbraith Laboratories, Inc., as follows:

N, N'-dibenzylhexaphenylcyclotrisilazane: Found, 787 and 802, average 794 (theory 772.1).

NMR spectra of Fraction 2 indicated that it was N-benzylhexaphenylcyclotrisilazane; the ratio of Si-phenyl to N-benzyl groups was 6:1 (theory for the N-benzyl derivative, 6:1). The elemental composition was:

Found: Carbon, 75.23%; hydrogen, 6.00%; nitrogen, 5.82%; silicon, 11.8%

Calculated: Carbon, 75.72%; hydrogen, 5.76%; nitrogen, 6.16%; silicon, 12.36%

The yield was 3.9% of theory. The molecular weight as determined by Galbraith was:

N-benzylhexaphenylcyclotrisilazane: Found, 768 and 781, average 774 (theory 682.0).

Evidently Fraction 2 was not pure N-benzylhexaphenylcyclotrisilazane.

To make Polymer 4, Figure 1, N, N'-dibenzylhexaphenylcyclotrisilazane was polymerized by heating at 380°C in air for 30 hours. At 380°C the product could not be poured. At room temperature, it was a benzene-soluble, black, brittle solid. When heated on a spatula, it fused and evolved gas to form a brittle solid that was apparently stable. Brittle fibers were pulled from the melt while it was fused.

Another sample heated at 240°C for 6 hours at 155 mm pressure apparently did not polymerize to a significant extent.

5. Attempt to prepare the acetyl derivative of hexaphenylcyclotrisilazane

The properties of the acyl derivatives of silazanes have not been described in the literature. We reasoned that if they were stable, it would be possible to prepare a number of interesting materials by treating the potassium derivatives of silazanes with mono- and difunctional acyl chlorides. Preparation of the acetyl derivative of hexaphenylcyclotrisilazane was chosen first as the simplest reaction leading to an evaluation of the acyl derivatives.

In a 200-ml, 3-neck, round-bottom flask fitted with a stirrer, dropping funnel, reflux condenser, and thermometer were placed 40 ml of purified dioxane and 0.73 g (0.0186 mole, 10% excess) of potassium. Then 10.0 g (0.0169 mole) of hexaphenylcyclotrisilazane in 70 ml of dioxane was added. Stirring was continued for an hour while the dioxane was refluxed and the potassium dissolved completely. The solution was cooled to room temperature, and 1.31 ml (1.45 g, 0.0185 mole) of acetyl chloride was added dropwise with stirring. The color changed from clear yellow to dark red-brown as the mixture became more viscous, and the temperature rose 20°C. The mixture was refluxed for an hour. Some solid gel was present. Most of the dioxane was removed by distillation, and attempts were made to separate the residue into its components by fractional crystallization from toluene and Skellysolve "B". About 80% of the theoretical amount of potassium chloride was eventually isolated, and 53% of the hexaphenylcyclotrisilazane was recovered, but there was probably more in the mother liquors. The residue obtained by evaporation of the mother liquors was 3.5 g of sticky resin. It appears that the reaction between the potassium derivative of hexaphenylcyclotrisilazane and acetyl chloride was not the desired simple addition.

6. N-Alkyl derivatives of hexaphenylcyclotrisilazane

a. N-Methylhexaphenylcyclotrisilazane

Two reactions were conducted in attempts to prepare N-methylhexaphenylcyclotrisilazane. The reactions differed in that the first was refluxed at 100°C, while the second was kept below 40°C after the addition of methyl iodide. The crystalline material recovered from each reaction had essentially the same melting-point range, but a higher proportion of the second product was crystalline.

The procedure for the second reaction follows: In a 200-ml, 3-neck, round-bottom flask fitted with a magnetic stirrer, thermometer, reflux condenser, and dropping funnel were placed 40 ml of purified dioxane and 0.73 g (0.0186 mole, 10% excess) of potassium. The liquid was stirred and heated to 75°C to disperse the potassium. Then 10.0 g (0.0169 mole) of hexaphenylcyclotrisilazane dissolved in 70 ml of dioxane was added. Stirring was continued while the mixture was refluxed for 2.5 hours to allow most of the potassium to react. The solution was cooled to room temperature, and 1.15 ml (2.615 g, 0.0184 mole, 9% excess) of recently distilled methyl iodide dissolved in 10 ml of purified dioxane was added with stirring, over a period of 15 minutes. A white solid formed, giving the solution a cloudy appearance, and the temperature rose 5°C. The mixture was stirred and warmed slightly, but the temperature was kept below 40°C for 3.5 hours. It was then cooled to room temperature, and the potassium iodide was filtered off. About 92% of the theoretical amount of potassium iodide was recovered. The dioxane was removed by distillation at reduced pressure, with the temperature of the pot kept below 40°C.

The residue, a soft, tan, partially crystalline material, was dissolved in benzene, and 8.49 g of crystals in several batches having a melting-point range of 149-210°C were recovered by recrystallization from mixtures of benzene and Skellysolve "B". The residue obtained by evaporation of the mother liquor was 1.46 g of a cloudy, yellow, viscous substance.

NMR spectra indicated that the crystalline material was a mixture of mono-, di-, and trimethyl substituents combined with some hexaphenylcyclotrisilazane. Attempts to fractionate these crystals by washing with Skellysolve "B" and recrystallizing from benzene produced no fraction of narrow melting-point range. It was then decided to mix 3.75 g of the lower-melting batches having a melting-point range of 159-197°C and submit these for NMR and infrared analyses and hydrolytic stability and polymerization evaluations.

NMR spectra again indicated three different types of protons in the crystals. This was formerly attributed to the presence of a mixture of mono-, di-, and trimethyl substituents. However, the three types of protons in both samples were in almost equal amounts. Consequently, it seems more likely that each of the three protons was responding individually in the NMR spectrum, and that the di- and tri-substituted materials were not present. The methyl protons were probably being split into a triplet by the nitrogen atom.

Infrared spectra indicated that little or no hexaphenylcyclotrisilazane was present. Elemental analysis gave the following results:

Found: Carbon, 72.43%; hydrogen, 5.78%; nitrogen, 6.50%; silicon, 13.0%

Calculated for N-methyl: Carbon, 73.33%; hydrogen, 5.84%; nitrogen, 6.93%; silicon, 13.9%

When polymerization was attempted by heating, the sample became black at 220°C. It was heated to 480°C, and then, on cooling, it solidified at about 100°C. On reheating to 520°C and cooling, it solidified at 240°C. On reheating, the mass foamed and became a friable black powder (Polymer 7, Figure 1).

The procedure for determining the hydrolytic stability was the same as previously reported.[21] The data are given in Section XI. The methylated compound was more stable than hexaphenylcyclotrisilazane, and so it appears that methyl substitution had a stabilizing effect.

b. N,N',N''-trimethylhexaphenylcyclotrisilazane

In a 200-ml, 3-neck, round-bottom flask equipped with a magnetic stirrer, thermometer, reflux condenser, and dropping funnel were placed 40 ml of purified dioxane and 2.18 g (0.0558 mole, 10% excess) of potassium. The mixture was stirred and warmed to 65°C to disperse the potassium. Then 10.0 g (0.0169 mole) of hexaphenylcyclotrisilazane dissolved in 50 ml of dioxane was added. Stirring was continued while the mixture was refluxed 4.0 hours to allow most of the potassium to react. The solution became dark red. It was cooled to room temperature, and 3.44 ml (7.85 g, 0.0553 mole, 9% excess) of recently distilled methyl iodide dissolved in 10 ml of purified dioxane was added with stirring over a period of 45 minutes. A white solid formed, giving the solution a cloudy appearance, and the temperature rose to 40°C. The mixture was stirred, and heat was added to keep the temperature at 35-40°C for 30 minutes; then it was cooled to room temperature, and the potassium iodide was filtered off. About 94% of the theoretical amount of potassium iodide was recovered. The dioxane was removed by distillation at reduced pressure, while the temperature of the pot was kept below 40°C.

The residue was a soft, yellow-orange, partially crystalline, semi-solid material. Recrystallization from mixtures of benzene and Skellysolve "B" yielded 6.97 g of crystals in several batches (m. p. 178-212°C) and 3.45 g of a soft resinous solid.

NMR spectra indicated that the ratio of phenyl protons: to methyl protons : to N-H protons was 30 : 3.5 : 3 in the batch of crystals that melted at 194-198°C. The expected ratio in the N-methyl compound would be 30 : 3 : 2. The elemental composition of the same fraction was:

Found: Carbon, 72.24%; hydrogen, 5.94%; nitrogen, 6.43%; silicon, 12.7%.

Calculated for N-methyl: Carbon, 73.33%; hydrogen, 5.84%; nitrogen, 6.93%; silicon, 13.9%.

The di- and tri- derivatives would have contained more carbon. Evidently the compound was not a pure mono-, di-, or trimethyl derivative. When the methyl derivative was heated in the manner that has been used to polymerize hexaphenylcyclotrisilazane, it blackened and charred without forming a viscous material that appeared to be a polymer.

c. N-Butylhexaphenylcyclotrisilazane

The attempt to prepare N-butylhexaphenylcyclotrisilazane did not produce a pure compound, but reaction occurred to form a mixture of compounds that probably were N-butyl derivatives.

In a 200-ml, 3-neck, round-bottom flask equipped with magnetic stirrer, thermometer, reflux condenser, and dropping funnel were placed 40 ml of purified dioxane and 0.73 g (0.0183 mole, 10% excess) of potassium. Then 10.0 g (0.0169 mole) of hexaphenylcyclotrisilazane in 70 ml of dioxane was added. Stirring was continued while the mixtures were refluxed for 4 hours, and most of the potassium dissolved. The solution was cooled to room temperature, and 2.10 ml (3.39 g, 0.0184 mole, 9% excess) of 1-iodobutane in 10 ml of purified dioxane was added dropwise with stirring. Heat was added, and the solution began to turn cloudy at 70°C. It was allowed to reflux at 100°C for 2.5 hours. At the end of this time a white solid, potassium iodide, was filtered out. About 65% of the theoretical amount of potassium iodide was recovered. The dioxane was removed by distillation, and the residue was a viscous, yellow, partially crystalline mixture. The mixture was dissolved in 25 ml of benzene, and 3.20 g of crystals, m.p. 195-212°C, was obtained by recrystallization. These were probably hexaphenylcyclotrisilazane. The mother liquor was then evaporated to dryness leaving a sticky resinous product weighing 8.20 g. An attempt was made to distill this at low pressure (0.01-0.02 mm). However, the product evolved a low-boiling material without distilling. Heating was continued for about 5 hours. Samples were withdrawn at 30-minute intervals throughout the process. These samples could be drawn into long, brittle fibers indicating polymerization. The softening points of these samples ranged from 56°C at the beginning of the process to 95°C when the polymerization was terminated. The pot temperature at the end of the process was about 200°C. The temperature was then increased in an attempt to force distillation, but extensive decomposition occurred, and a char was obtained.

d. N, N', N''-tributylhexaphenylcyclotrisilazane

The attempt to prepare the tributyl derivative of hexaphenylcyclotrisilazane was carried out in the same manner as the reaction just described except that the amounts of potassium and 1-iodobutane were tripled. The product was a semisolid, and recrystallization of it yielded 4.65 g of crystals in several batches, m.p. 159-203°C, which were predominantly hexaphenylcyclotrisilazane, and 6.4 g of red, oily liquid that crystallized on standing overnight. The latter appeared by NMR spectra to be a crude mixture with some polymeric material. It did not appear to be worthy of evaluation as a lubricant because of crystallization. Coatings applied to aluminum had thermal stability comparable to that of the other silazanes.

e. N-Octadecylhexaphenylcyclotrisilazane

An attempt to prepare the N-octadecyl derivative of hexaphenylcyclotrisilazane was carried out as follows: In a 200-ml, 3-neck, round-bottom flask fitted with a thermometer, reflux condenser, magnetic stirrer, and dropping funnel were placed 30 ml of purified dioxane and 2.18 g (0.0558 mole) of potassium. The flask was flushed with nitrogen, the liquid was heated with stirring to 60°C, and hexaphenylcyclotrisilazane, 10.0 g (0.0169 mole) dissolved in 50 ml of dioxane, was added. The mixture was refluxed for 4 hours which caused all but a trace of the potassium to dissolve. The liquid was cooled to room temperature, and 21.03 g (0.0553 mole) of 1-iodooctadecane in 50 ml of dioxane was added, whereupon the temperature rose 8°C. The mixture was then stirred at 36-38°C for 2 hours. A large amount of solid, presumably potassium iodide, appeared in the solution. The product was cooled and filtered, and the precipitate was washed with dioxane. When free of solvent, the precipitate weighed 7.35 g (80% of the theoretical amount of potassium iodide).

The dioxane was distilled from the filtrate at reduced pressure, and the residue was a tan solid in a red-orange liquid. The suspension was filtered, and the solid portion was found to weigh 8.3 g. When an attempt was made to determine its melting point, it appeared to decompose at 160-165°C. An attempt was made to distill the liquid. Part of it distilled at 105-119°C at 0.1 mm, and carbon-hydrogen analysis indicated that the distillate was largely a hydrocarbon. The remainder was a soft solid. It was apparent that the reaction was complex and that no appreciable amount of a liquid derivative of hexaphenylcyclotrisilazane was produced. Hence, no further work was done on the octadecyl derivative.

f. N-Decylhexaphenylcyclotrisilazane

Potassium and n-decyl iodide were used in an attempt to prepare a decyl derivative of hexaphenylcyclotrisilazane. The method and results were similar to those just described.

VIII. CURING PROPERTIES OF METHYLHYDROGENSILYLAMINES

A. Discussion

Silylamines made from chlorosilanes with silicon-hydrogen bonds were investigated previously and found to polymerize at unusually low temperatures,[22,23] but the polymers were brittle and not outstandingly stable. The work was resumed in an effort to promote low-temperature curing of coatings by mixing methylhydrogensilylamines with other silylamines. The curing conditions were made milder, but brittleness was increased. At present, it is not possible to decide whether the simplification of curing is sufficient to offset the loss of performance, because the competing effects cannot be judged in relation to a specific end use. Whenever work is intensified for a specific application, the use of methylhydrogensilylamines should be reexamined.

The methylhydrogensilylamines were made by treating methyldichlorosilane with ammonia or methylamine in the presence of triethylamine. The methylamine derivative performed better. When it was added at the level of 5% and 10% to the boiled methylphenyl silazane-TEA described in Section IV it promoted curing of a coating on aluminum in 1.75 hours at 190°C to a hard film that did not flow when heated to 400°C. Under similar conditions such a coating without the methylhydrogen compound would have softened enough to flow when first heated to 400°C. In 2-3 hours at 400°C 2-mil coatings that contained the methylhydrogen compound flaked off, whereas coatings without the methylhydrogen compound would have lasted 18 hours or more.

B. Experimental Details

1. Preparation and curing properties of methylhydrogen methylamino silazane-TEA

In a 500-ml, 3-neck flask equipped with stirrer, reflux condenser, thermometer, and gas-inlet tube were placed 200 ml of benzene, 101.2 g (1.0 mole) of triethylamine and 57.5 g (0.5 mole) of methyldichlorosilane. This mixture was stirred for 0.75 hour. Methylamine, dried over sodium, was passed over the stirred solution for 5 hours, while the temperature was kept below 30°C. The salt was filtered off, and the solution was refluxed for

1.5 hour. The benzene and triethylamine were removed at reduced pressure. The final product was 44.1 g of clear, colorless liquid. The yield was 120% of theory if the formula was assumed to be $-(CH_3)HSiNCH_3-$, which is the formula for a cyclic structure. Obviously, the assumed formula was not correct. NMR spectra showed that the ratio of protons in SiH, NCH_3, and NH + $SiCH_3$ groups was 1 : 3.7 : 3.3. In the assumed formula, above, the ratio of protons is 1 : 3 : 3. If a linear structure was assumed, $HCH_3N-(SiHCH_3NCH_3)_n-H$, the actual yield was 95% of theory when n = 3, and the theoretical ratio of protons was 1 : 4 : 3.7. It seems likely that the product was a mixture of linear and cyclic compounds. It is designated the "methylhydrogen methylamino silazane-TEA."

The clear liquid product, 10%, and boiled methylphenyl silazane-TEA, 90%, were mixed, spread on an aluminum panel, and heated in air at 190°C for 1.75 hour. When cool, the coating, which was 2 mils thick, was hard and tightly adhered. When the coating was heated again to 400°C with the panel in a non-level position, it did not flow. Such a coating without the methylhydrogen compound would have flowed slightly at 400°C. On further heating at 400°C the panel flaked in 2 hours. A similar coating with only 5% of the methylhydrogen compound performed the same except that it did not flake until it had been at 400°C for 3 hours.

2. Preparation and curing properties of methylhydrogen silazane-TEA

In a 1-liter, 3-neck flask equipped with stirrer, reflux condenser, thermometer, and gas inlet tube were placed 400 ml of benzene, 101.2 g (1.0 mole) of triethylamine, and 57.5 g (0.5 mole) of methyldichlorosilane. The solution was stirred for 30 minutes; and then ammonia, dried over sodium, was passed over the stirred solution for 3 hours. After the reaction with ammonia was apparently complete, the solution was refluxed for 3 hours. The salt was filtered off, and the benzene and triethylamine were distilled from the reaction. The product was 34.1 g of liquid (116% of the theoretical yield if $-SiHCH_3NH-$, the cyclic structure, is assumed as the formula). This material is designated the "methylhydrogen silazane-TEA."

Performance of the methylhydrogen silazane-TEA as a curing agent for coatings was appreciably poorer than that of the methylhydrogen methylamino silazane-TEA. When it was used in 10% concentration with methylphenyl silazane-TEA, the coating flaked off the aluminum panel in 1 hour at 190°C.

IX. POLYMERIZATION OF TRI- AND TETRAAMINOSILANES

A. Discussion

The ability of triethylamine to inhibit cyclization of silazanes presented a possible new route for making desirable polymeric silazanes from tri- and tetrachlorosilanes. Earlier work[24] did produce polymers, but none had high enough molecular weight to have good strength properties, and they had low softening points. The closest approach to a desirable polymer of this type was made by the reaction of methylamine with a mixture of silicon tetrachloride and methyltrichlorosilane. The initial reaction product was heated to 380°C while gaseous products were evolved; and, on cooling, it formed a resinous, colorless, brittle solid, that softened at 150-175°C. Further heating caused it to foam to a brittle, infusible solid.

In the present work the mixture of silicon tetrachloride and methyltrichlorosilane was treated with methylamine in the presence of triethylamine. As before, the liquid product evolved a gas, probably largely methylamine, when it was heated. As heating was prolonged, the viscosity increased, and finally the mass became solid and infusible while foaming. Efforts were made to terminate the reaction just before the final solidification, but no resinous solid with a softening point above 100°C was obtained.

The prepolymer made from methyltrichlorosilane and silicon tetrachloride when added in 10% concentration increased the curing rate of a coating made from methylphenyl silazane-TEA, but caused it to be more brittle.

B. Experimental Details

1. Method of preparation and polymerization

The reaction of methylamine with a mixture of methyltrichlorosilane and silicon tetrachloride in the presence of triethylamine was conducted as follows:

In a 2-liter, 3-neck flask equipped with stirrer, reflux condenser, thermometer, and gas-inlet tube were placed 37.4 g (0.25 mole) of methyltrichlorosilane, 31.9 g (0.19 mole) of silicon tetrachloride, 305.6 g (3.02 moles) of triethylamine, and 600 ml of benzene. The solution was stirred for 30 minutes. Methylamine, dried over sodium, was passed over the stirred reaction for 4 hours. After the reaction with methylamine was apparently complete, the solution was refluxed for 1.5 hour. The salts were filtered off, and the benzene and triethylamine were distilled from the reaction. The product was 36.3 g of a cloudy, yellow, liquid resin.

Several attempts to form a high-melting resin by rapid heating in a test tube failed, because the transition from a low-melting solid to an infusible solid occurred quickly and without a visible preliminary indication. Consequently, a portion of the cloudy, yellow liquid resin was placed in a flask and heated slowly for about 16 hours in a nitrogen atmosphere. Evolution of gas started as usual at about 100°C. After 7.5 hours of heating, the mass was cooled, and it remained liquid at room temperature. After another 8 hours of heating at gradually increasing temperature, the melt was evolving gas quietly at 210°C. On being cooled to room temperature it solidified. When heating was resumed, it melted at about 100°C and evolved gas slowly when it reached 310°C. Within 15 minutes it solidified to a brittle, pale yellow, foamed, infusible mass. It appears that the infusible state is reached while the molecular weight is still low. Consequently, the probability that a tough high-melting solid can be produced by this method is quite low.

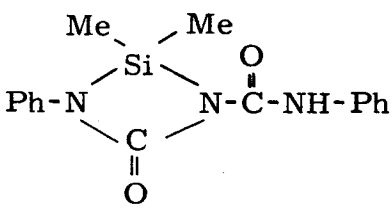
2. Curing properties in coatings

The cloudy, yellow, liquid resin (made from methylamine, silicon tetrachloride, methyltrichlorosilane, and triethylamine) was tried as an aid to the curing of a coating made with methylphenyl silazane-TEA (Section IV). The resin was boiled gently in a test-tube at 300°C for 5 minutes. Then it was mixed, 10%, with the boiled methylphenyl silazane-TEA described in Section IV.B.1.a. It was spread on an aluminum panel to form a smooth coating, and after 2 hours at 190°C it was hard and well adhered to the panel. It did not flow when placed vertically in an oven at 400°C. The coating flaked off the panel in 70 minutes at 400°C.

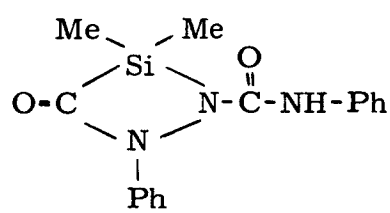
X. REACTION OF HEXAMETHYLCYCLOTRISILAZANE WITH PHENYL ISOCYANATE

A. Discussion

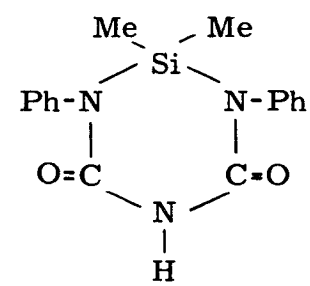
Isocyanates have been known to react with silicon-nitrogen compounds having -NH groups, but the products have not been characterized.[25, 26] In an effort to determine whether the isocyanate derivatives were worth further effort, the reaction between hexamethylcyclotrisilazane and phenylisocyanate was investigated. Reactions in 3 : 1 to 1 : 7 mole ratios resulted in crystalline materials. It appears that the reaction disrupted the silazane molecule, and that 2 moles of isocyanate reacted with each Si-N unit. According to elemental composition and molecular weight, at least three different formulas for the products are possible.



A

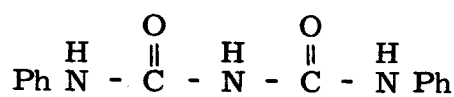


B



C

Formulas A and B could have resulted from an initial reaction of 3 molecules of phenylisocyanate with the three N-H groups of hexamethylcyclotrisilazane in the conventional manner. The product could then have split into three parts, each of which reacted with another isocyanate by simple addition. The mechanism of formation of a compound having Formula C is not easily explained. However, NMR spectra indicated a high order of similarity in the phenyl groups which suggested symmetry in the molecule. C is more symmetrical than A, which is more symmetrical than B. Infrared spectra indicated that there are two different carbonyls in the molecule, favoring A or B. B would have to result from attachment of the carbonyl of the isocyanate to the silicon of the SiN unit, and this seems less likely than attachment of the carbonyl to the nitrogen. Attempts were made to hydrolyze the crystalline compound to identifiable quantities of aniline or phenylhydrazine, but they were not successful. The hydrolysis product melted at about the same temperature as the starting material. The hydrolysis product could have been a compound such as diphenylbiuret,



which could be derived from either A or C.

After the work described was done, information was obtained from Fink[27] that he had identified the product by X-ray analysis as having Formula C. Consequently, no further work was done. It is clear that isocyanate disrupted the ring and that the product was not stable enough to serve our purpose.

B. Experimental Details

Several reactions were run in an effort to isolate and study an isocyanate derivative of hexamethylcyclotrisilazane. In the reactions, one mole of hexamethylcyclotrisilazane was treated with $\frac{1}{3}$, 1, 3, and 7 moles of phenyl isocyanate. Reactions with the two lower proportions of isocyanate produced a small amount of crystalline material melting in the range of 170°C, but the yields were low, and isolation of the products was complicated by the presence of a large amount of moisture-sensitive material. The reaction with 3 moles was conducted as follows: In a 50-ml, 3-neck, round-bottom flask equipped with a reflux condenser, thermometer, and magnetic stirrer were placed 20 ml of benzene and 6.57 g (0.03 mole) of hexamethylcyclotrisilazane. Then 11.90 g (0.10 mole) of phenylisocyanate was added rapidly with stirring. The temperature rose to 80°C, but no other evidence of reaction was apparent. Suddenly, after about 10 minutes of stirring, the reaction mixture crystallized. An additional 10 ml of benzene was added, and stirring was continued for a total of 3 hours. No external heat was applied.

A sample of the crystals was separated and recrystallized from Skellysolve "B". It melted at 210-213°C. After extensive fractional crystallization from dioxane, several batches of crystals were obtained with melting points ranging from 184-216°C. One of the batches, m.p. 203-204°C, was analyzed with the following results:

Found: Carbon, 61.83%; hydrogen, 5.69%; nitrogen, 13.72%; silicon, 8.9%; oxygen (remainder), 9.86%.

Calculated for $C_{16}H_{17}N_3O_2Si$ (Formula A, B, or C, page 89): Carbon, 61.71%; hydrogen, 5.50%; nitrogen, 13.49%; silicon, 9.02%; oxygen, 10.28%.

Molecular weight: Found, 346 and 359, average 353 (vapor osmometry, Galbraith Laboratories, Inc.)

Calculated, 311.4

The analysis indicated that two moles of phenyl isocyanate, C_6H_5CNO, had combined with each $-(CH_3)_2SiNH-$ unit. Accordingly, another reaction was run in which 7 moles of isocyanate was added for each mole of hexamethylcyclotrisilazane. The actual quantities were 2.46 g (0.0112 mole) of hexamethylcyclotrisilazane and 8.92 g (0.075 mole) of phenyl isocyanate. After recrystallization, 4.85 g of crystals was obtained. When the melting point of the crystals was taken rapidly, it was 213-216°C; when taken more slowly, it was 207-208°C. When the melting point was observed on the hot stage of a microscope, a change in appearance, but no melting, of the crystals was observed over the range of 188°C-197°C. As the temperature was decreased to 160°C, changes in appearance continued, and on reheating liquid was seen at 178°C. Final melting occurred at 198°C. It was concluded that the compound underwent a change in crystal structure at temperatures above 160°C.

Several attempts were made to hydrolyze the unknown compound and identify fragments. If the compound had any of the three formulas, A, B, or C, it would be expected to yield aniline on hydrolysis. If it had Formula B, it would yield aniline and phenylhydrazine. If it had either Formula A or C, it would yield 2 moles of aniline and 1 mole of ammonia. It was expected that aniline or phenylhydrazine could be recognized by ultraviolet spectra.

The compound was recovered unchanged after shaking it with water and 30% aqueous sodium hydroxide. Then it was boiled with 6 N hydrochloric acid for 7.5 hours, and approximately half of it dissolved. The part that did not dissolve sintered at 199-201°C and turned brown. It may have been changed or made impure by the acid treatment, but it was not converted entirely to soluble material. The compound, 0.2 g, was dissolved in 5 ml of concentrated sulfuric acid at room temperature, and the solution was warmed on the steam bath for 2.5 hours. The colorless solution was then poured into 45 ml of water, and the resulting solution was clear and colorless. Neither acid-treated solution had the characteristic absorption spectra of aniline or phenylhydrazine. The work was terminated because of the report of Fink's identification[27] by X-ray analysis.

XI. EVALUATION OF HYDROLYTIC AND THERMAL STABILITIES OF SILYLAMINES

A. Discussion

1. Hydrolytic stability

Hydrolytic stabilities of new silicon-nitrogen compounds were determined in a continuing study of the factors that affect this property. Rates of hydrolysis were compared by dissolving each compound in benzene or carbon tetrachloride and shaking the solution with water or dilute acid. Previous findings were discussed in the preceding annual report.[28]

The silylamines most stable to hydrolysis are the N-benzyl, N, N'-dibenzyl, and N-trimethylsilyl derivatives of hexaphenylcyclotrisilazane. The N-methyl derivative of hexaphenylcyclotrisilazane that was not completely purified (Section VII. B. 6. a.) was more stable than hexaphenylcyclotrisilazane. Attachment of the benzyl, trimethylsilyl, and methyl groups stabilized the entire rings and not just the portions of the rings close to the substituent groups.

Octamethylcyclotetrasilazane was found to be more stable to hydrolysis than hexamethylcyclotrisilazane by a factor of 6. This difference was surprisingly great. It is becoming increasingly evident that the type of bonding in cyclic silazanes is not well understood.

2. Thermal stability

Differential thermal analysis (DTA) was used to study the thermal stability of several polymers derived from silylamines in comparison with several well-known high-temperature polymers from other sources. Comparisons were made in air.

The data obtained suggest that the phenylene-bridged elastomer of Section V possesses a degree of thermal stability in air that is comparable with that of polybenzimidazole.

The polymers studied are listed in Table V. Following is the relative order of thermal stability of these polymers as indicated by DTA beginning with the least stable:

Viton B - destructive decomposition begins at 420°C

Teflon - destructive decomposition begins at 480°C

Polymer made from polymeric diphenylsilazane (Section III. B. 1) - destructive decomposition begins at 500°C

Dow Corning 803 (coating) - destructive decomposition begins at 500°C

Polymer made from the reaction of the methylphenyl silazane and p, p'-biphenol [Section VI. B. 1. a. (4)] - destructive decomposition begins at 540°C

DuPont's Pyre-M-L (polybenzimidazole) - destructive decomposition begins at 600°C

Phenylene-bridged elastomer (Section V) - destructive decomposition begins at 600°C.

B. Experimental Details

1. Method of measuring rate of hydrolysis

The method of comparing the rates of hydrolysis is described in an earlier report.[28] Briefly, the procedure is to dissolve 0.5-5 milliequivalents of the silicon-nitrogen compound in 50.0 ml of carbon tetrachloride, shake the solution with 100.0 ml of water, and titrate the water layer periodically to determine the amount of ammonia or amine present. Compounds difficult to hydrolyze are compared by adding an amount of hydrochloric acid equivalent to the silazane to the water.

Hydrolysis of N-benzylhexaphenylcyclotrisilazane was observed by dissolving 0.2303 g (1.014 milliequivalents) in 50.0 ml of carbon tetrachloride and shaking the solution with 100.0 ml of water for 176 minutes. No detectable further hydrolysis was observed after 18 minutes, when the amount hydrolyzed was approximately 3%. At this point, to conserve the limited amount of compound, acid hydrolysis was started with the same solution. An amount of acid equivalent to the silazane was added, and the hydrolysis was observed for 145 minutes. At the end of that period, the amount hydrolyzed was 33%. The data are plotted in Figure 3, and the results are given in Table IV.

Detailed data are not presented for the hydrolysis of the N-benzyl compound in water because of the uncertainty of the distribution of benzylamine between carbon tetrachloride and water. However, there is no doubt that the extent of hydrolysis was small regardless of the distribution of benzylamine between solvent and water since the observed amount was only 3%. The uncertainty about distribution did not exist when acid was used.

After the prolonged hydrolysis of the N-benzyl compound with acid, the carbon tetrachloride layer was evaporated, and 0.1817 g of solid, m.p. 127-131°C (original compound, m.p. 154-156°C) was recovered. The amount expected was 0.129 g, representing the amount remaining after loss due to hydrolysis and the withdrawal of two samples of the organic solvent layer for titration.

Hydrolysis of N,N'-dibenzylhexaphenylcyclotrisilazane was observed by the same procedure with 0.1491 g (0.579 milliequivalent) of the silazane. Only 10% hydrolysis was detected in water in 205 minutes. Acid was added, and the hydrolysis was continued for 97 minutes. The hydrolysis with the acid was 15%. Evaporation of the carbon tetrachloride layer and recrystallization of the residue yielded 0.0768 g of the original compound, m.p. 163-166°C (original 168-169°C). The data are plotted in Figure 3, and the results are given in Table IV.

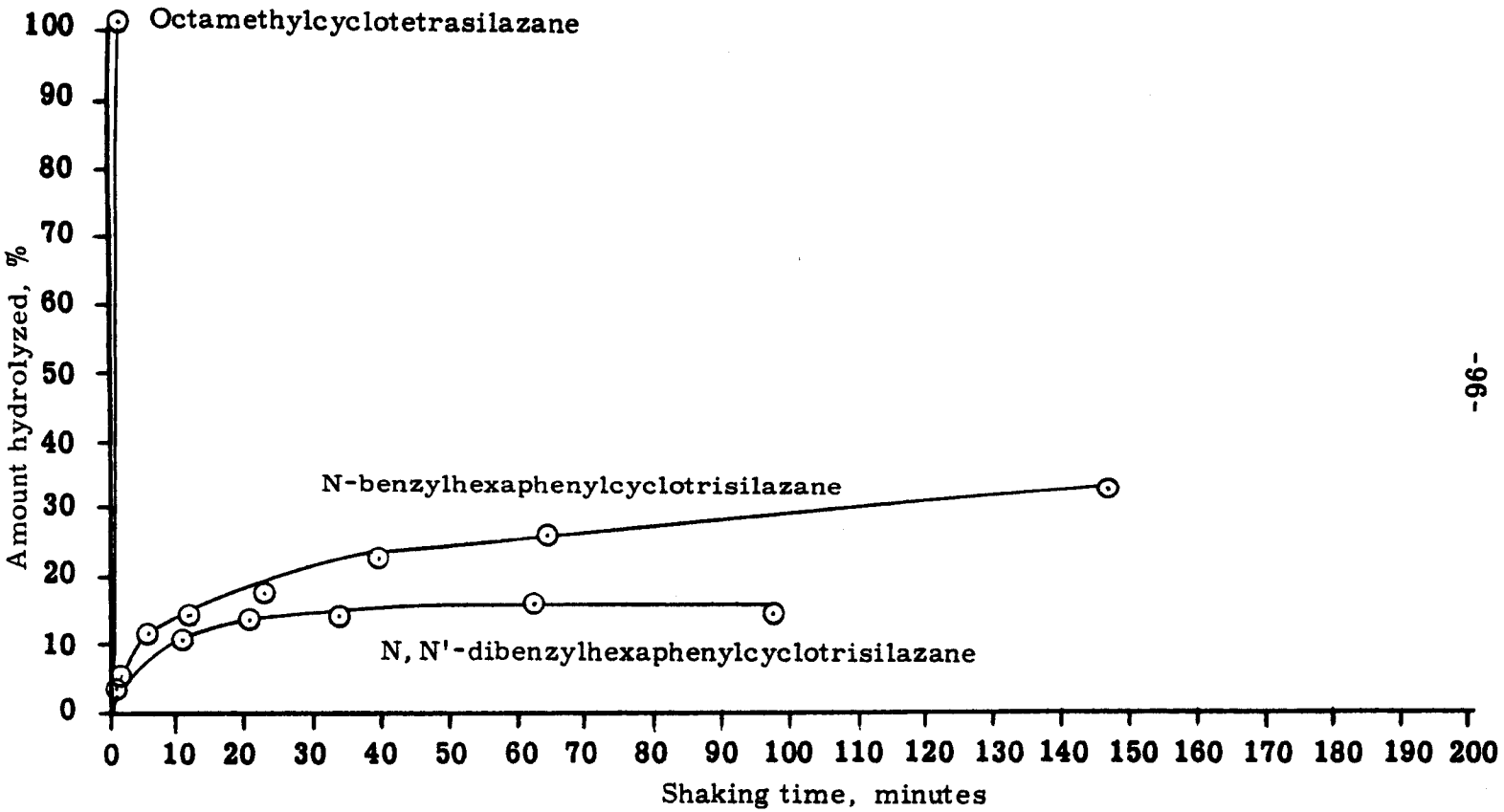


Figure 3. Hydrolysis in Carbon Tetrachloride with Hydrochloric Acid

Table IV. Relative Rates of Hydrolysis of Silylamines

	Solvent + H_2O			Solvent + H_2O + HCl		
	Time for 25% hydrolysis, min	Hydrolysis in first 20 min. %	Rate, % per hour	Time for 25% hydrolysis, min	Hydrolysis in first 20 min. %	Solvent
N,N'-Dibenzylhexaphenylcyclotrisilazane				—[a]	13	CCl_4
N-Trimethylsilylhexaphenylcyclotrisilazane				139	9	CCl_4
Mixed N-methyl derivatives of hexaphenylcyclotrisilazane		0.9		98	14	benzene
N-Benzylhexaphenylcyclotrisilazane				60	18	CCl_4
Hexaphenylcyclotrisilazane				5	42	benzene
Octamethylcyclotetrasilazane (average of two determinations)		3.8	2.2	< 1	100	CCl_4
Hexamethylcyclotrisilazane	23	23	38	< 1	100	CCl_4

[a] About 15% hydrolyzed in 100 minutes—further hydrolysis not detected after 30 minutes.

Hydrolysis of octamethylcyclotetrasilazane was observed by shaking 0.3725 g (5.1 milliequivalents) with carbon tetrachloride and water. In 50 minutes, 6% was hydrolyzed. In a second experiment, 3% hydrolyzed in 60 minutes. In the first, the unhydrolyzed octamethylcyclotetrasilazane was checked by titration of the organic layer; and, in the second experiment, 84% was recovered by evaporation and identified by melting point. In acid, 99% hydrolyzed in 1 minute. The data from hydrolysis in acid are plotted in Figure 3, and the data from water are plotted in Figure 4. The results are given in Table IV with data previously obtained on hexamethylcyclotrisilazane.[29]

The hydrolysis of the N-methyl derivative of hexaphenylcyclotrisilazane was observed when a benzene solution of it was shaken with water and hydrochloric acid. The results are in Table IV and Figure 5.

2. Method of differential thermal analysis

DTA measurements were made with a Robert L. Stone Company Model 13 M, differential thermal analysis apparatus. The methods of preparation and principal temperatures of endothermic and exothermic change are indicated in Table V and Figures 6-12.

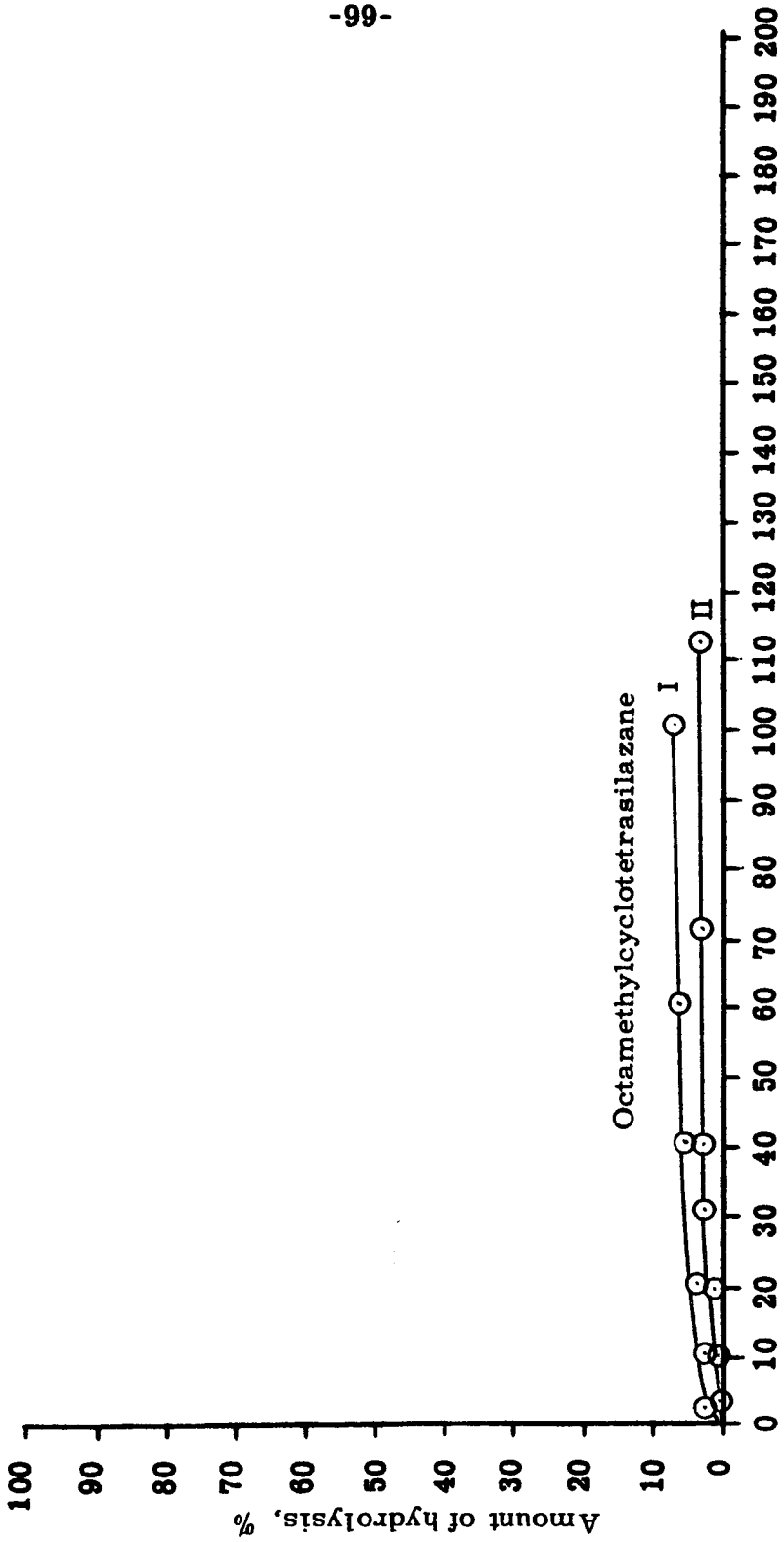


Figure 4. Hydrolysis in Carbon Tetrachloride and Water.

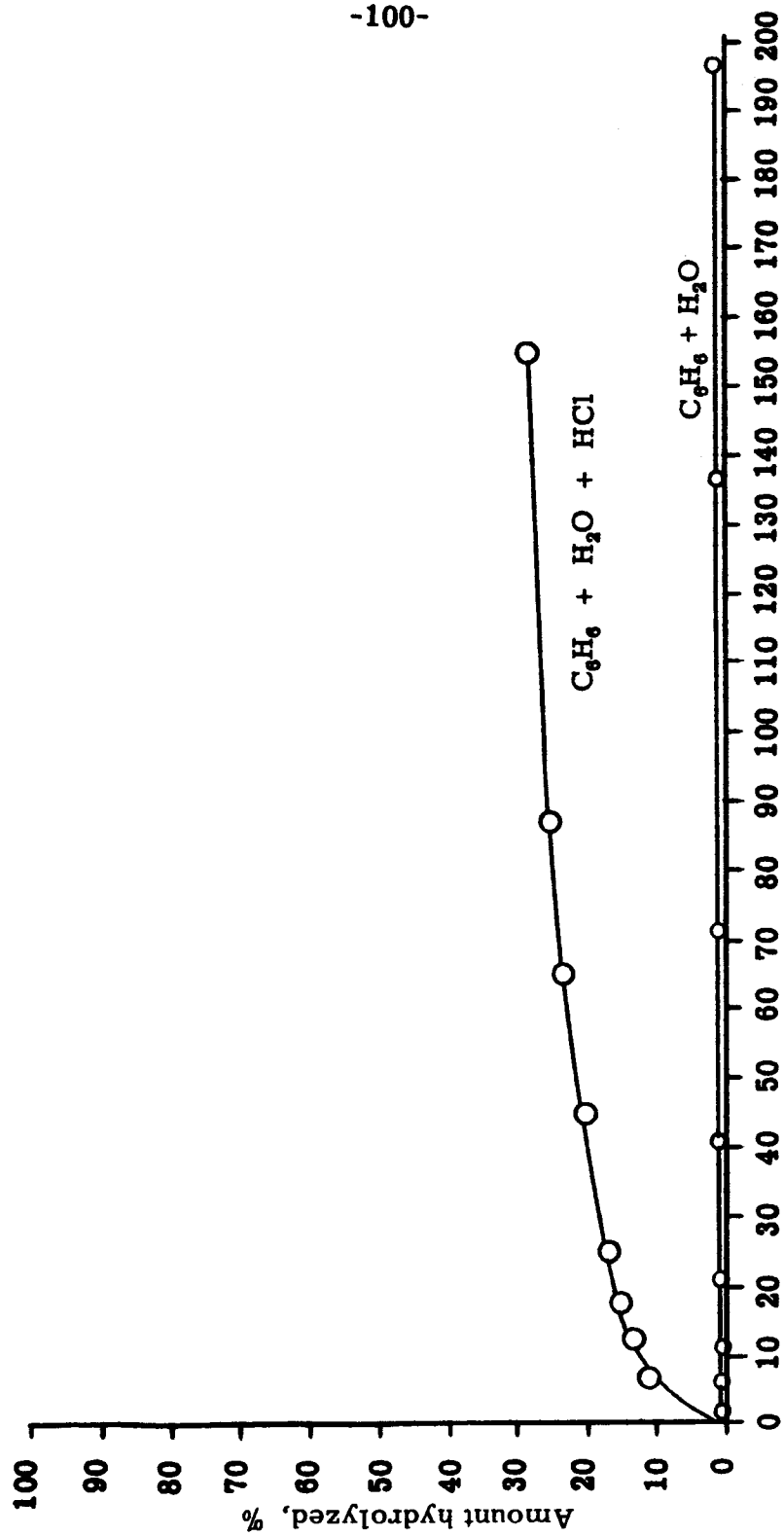


Figure 5. Hydrolysis of N-Methyl Derivative of Hexaphenylcyclotrisilazane.

Table V. Summary of Differential Thermal Analyses of Polymers (in air; temperature increase 10°C per minute)

Polymer	Preparation	Figure	Features of DTA curves	Interpretation
Viton B	As received	6	Moderate exothermic drift to 420°C strong exotherm, 420-460°C; moderate exotherm 460-560°C; strong exotherm, 560-600°C	Moderate loss in weight to 420°C; decomposition, 420-460°C, with fragments burning; rate change 460-560°C; additional rapid decomposition, 560-600°C
Teflon	As received	7	Moderate exotherm, 480-560°C	Decomposition from 480-560°C
Silicon-nitrogen	Polymeric diphenylsilazane (Section III. B. 1), heated 2 hours in air at 300°C, 16 hours at 350°C	8	Slight exotherm to 500°C; strong exotherm, 500-600°C	Decomposition from 500-600°C, with fragments burning
Siloxane	Dow Corning 803 resin, cast on Teflon, air dried 16 hours, heated to 450°C, stripped from mold	9	Slight exotherm to 500°C; moderate exotherm, 500-580°C	Decomposition from 500-580°C, with fragments burning
Silicon-nitrogen	Polymerized product of reaction of methylphenyl methylamino silazane and p, p'-biphenol [Section VI. B. 1. a. (4)], heated in air at 300°C for 4 hours	10	Slight exotherm to 540°C; strong exotherm, 540-620°C	Decomposition from 540-620°C, with fragments burning
Polybenzimidazole	DuPont Pyre-M-L, film cast and cured on steel plate at 260°C, then stripped	11	Slight exotherm to 550°C; slight endotherm, 550-570°C; moderate exotherm, 600-610°C; moderate endotherm, 610-620°C	Rearrangement, 550-570°C; decomposition at 600°C
Phenylene-bridged elastomer	Polymer made from product of reaction of methylamine with 1, 4-bis(dimethyl-chloro)silyl benzene (Sample 3205-55-4, Section V. B. 1. b.)	12	Sharp endotherm at 100; slight exotherm, 100-400°C; slight endotherm, 400-520°C; series of very small exotherms, 520-600°C; moderately strong exotherm, 600-630°C	Loss of crystallinity, 100°C; decomposition at 600°C

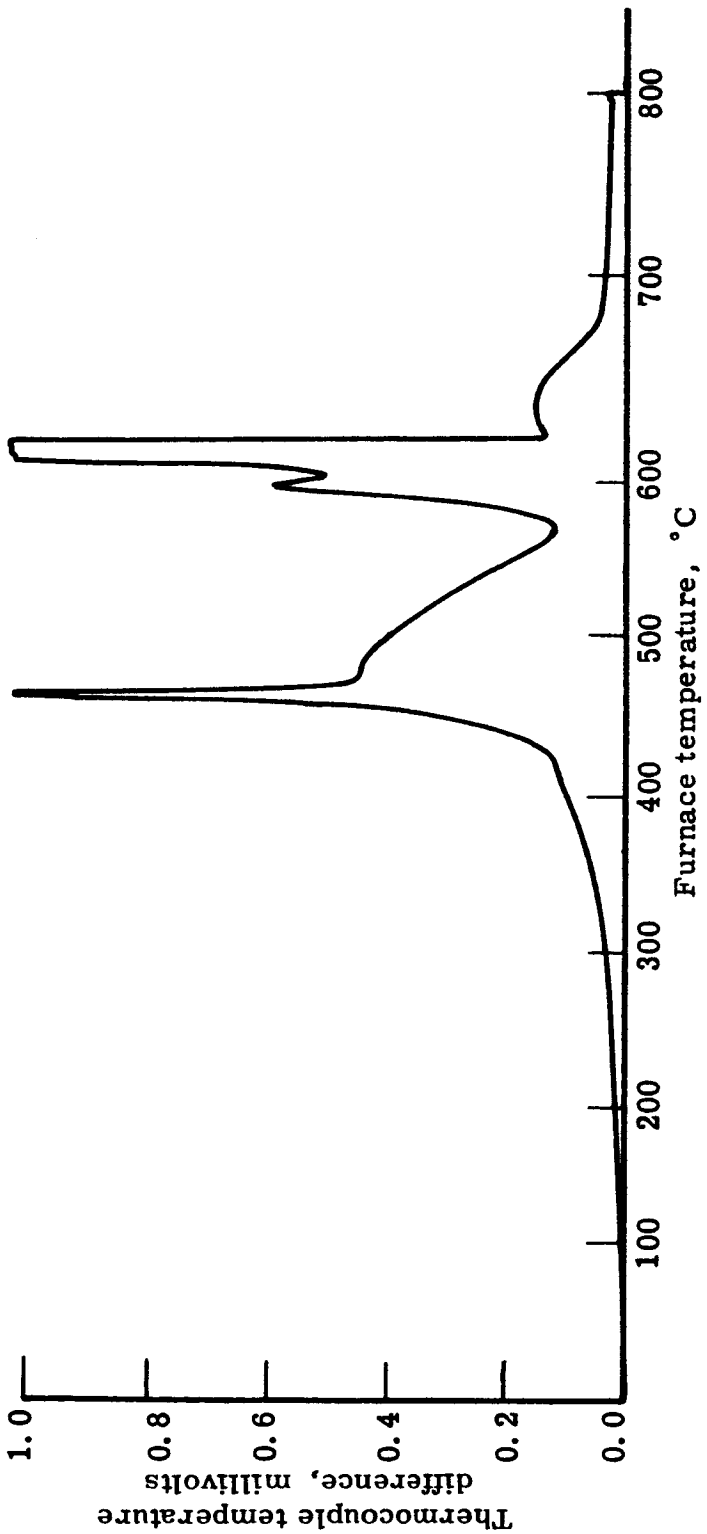


Figure 6. Differential Thermal Analysis of Viton B.

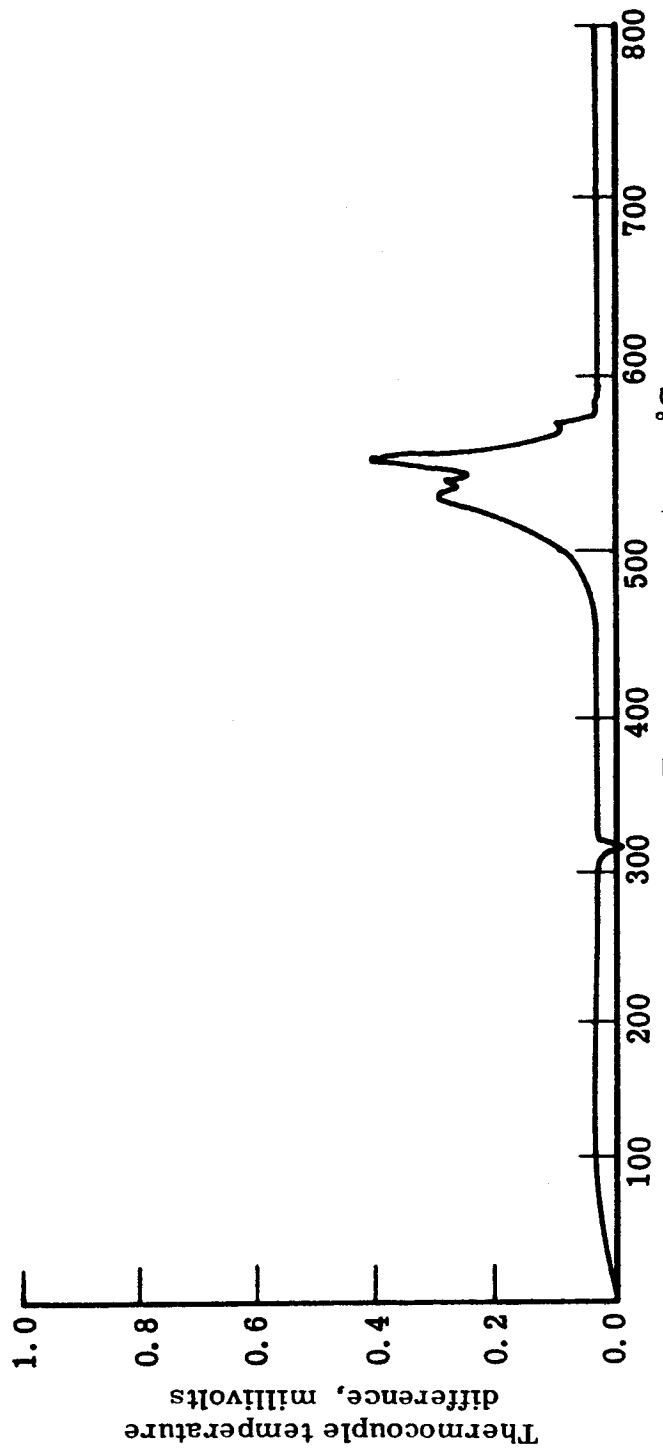


Figure 7. Differential Thermal Analysis of Teflon

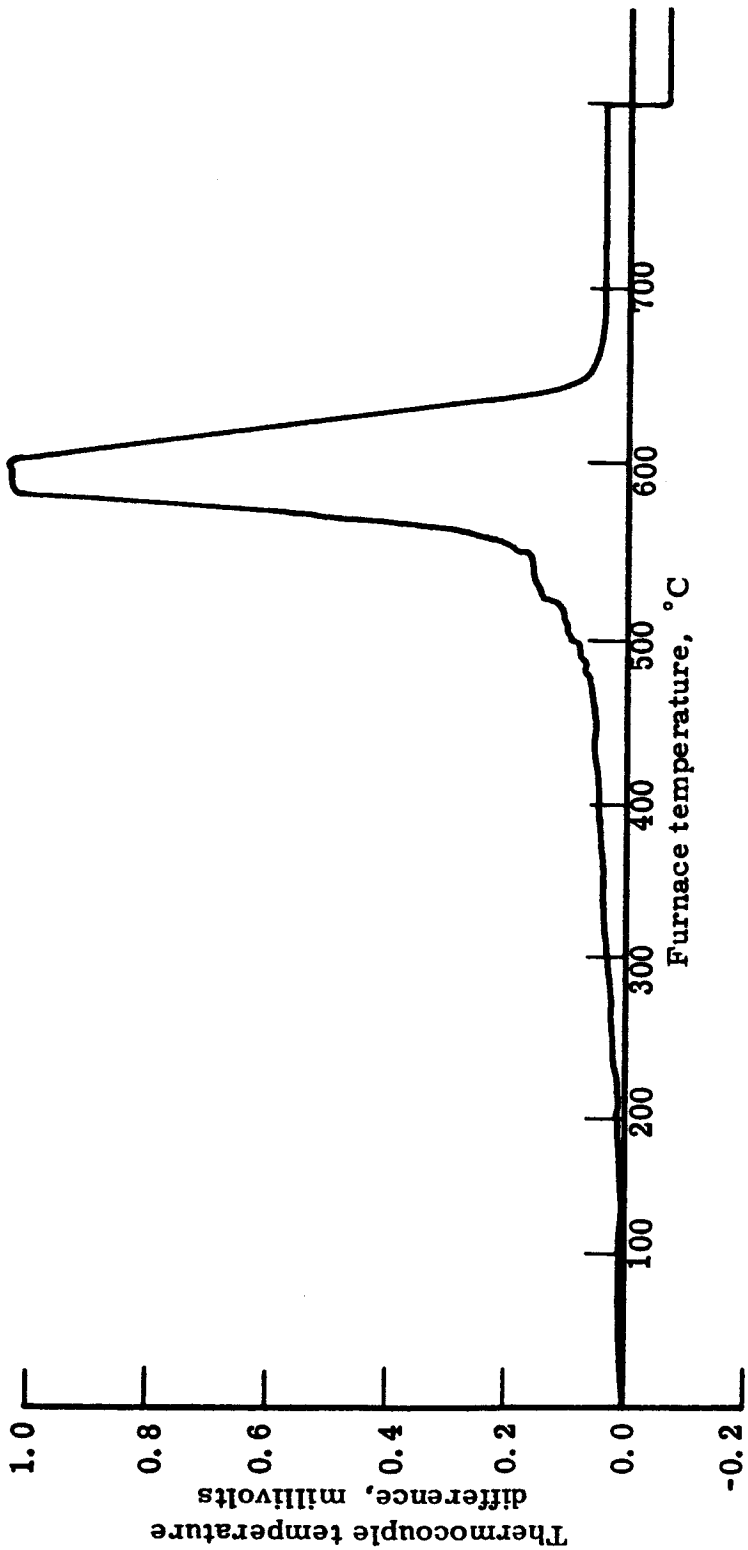


Figure 8. Differential Thermal Analysis of Polymer Made from Polymeric Diphenylsilazane (Section III. B. 1).

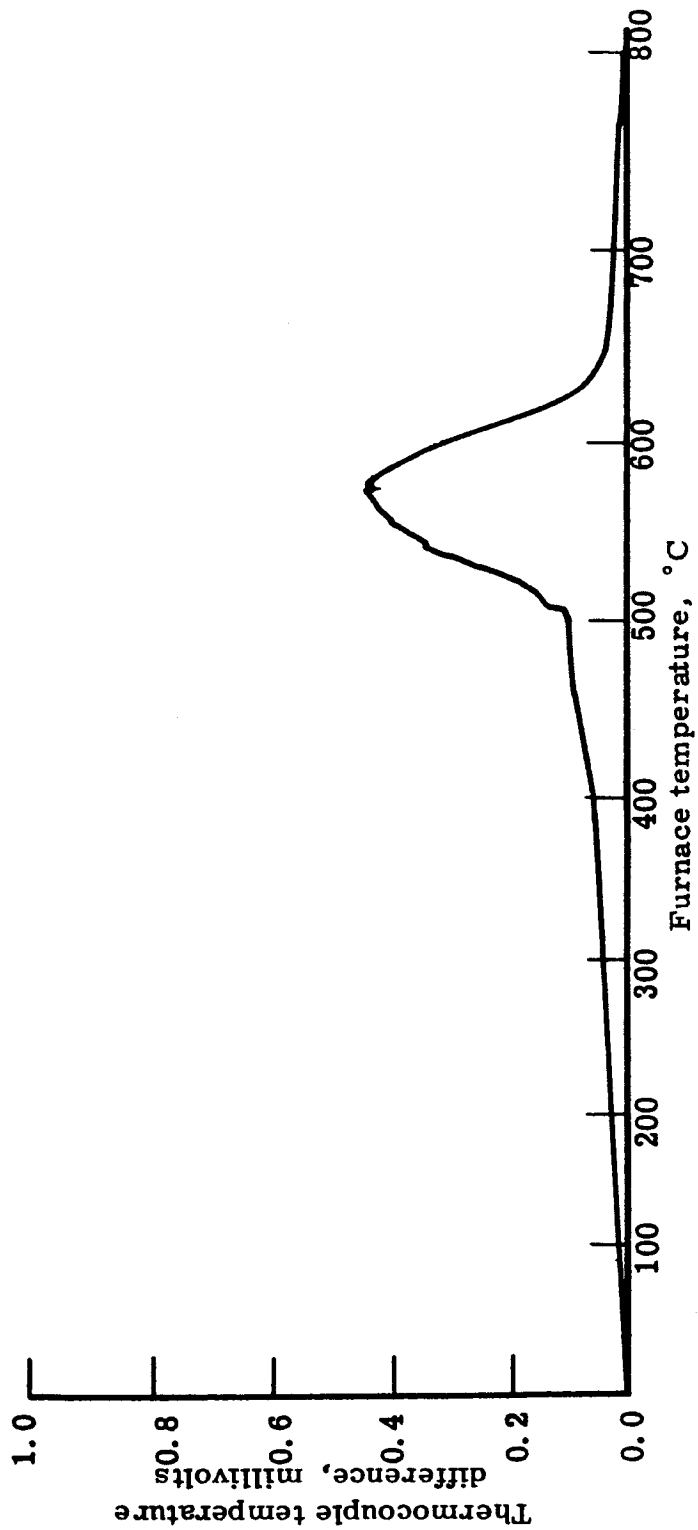


Figure 9, Differential Thermal Analysis of Coating, Dow Corning 803.

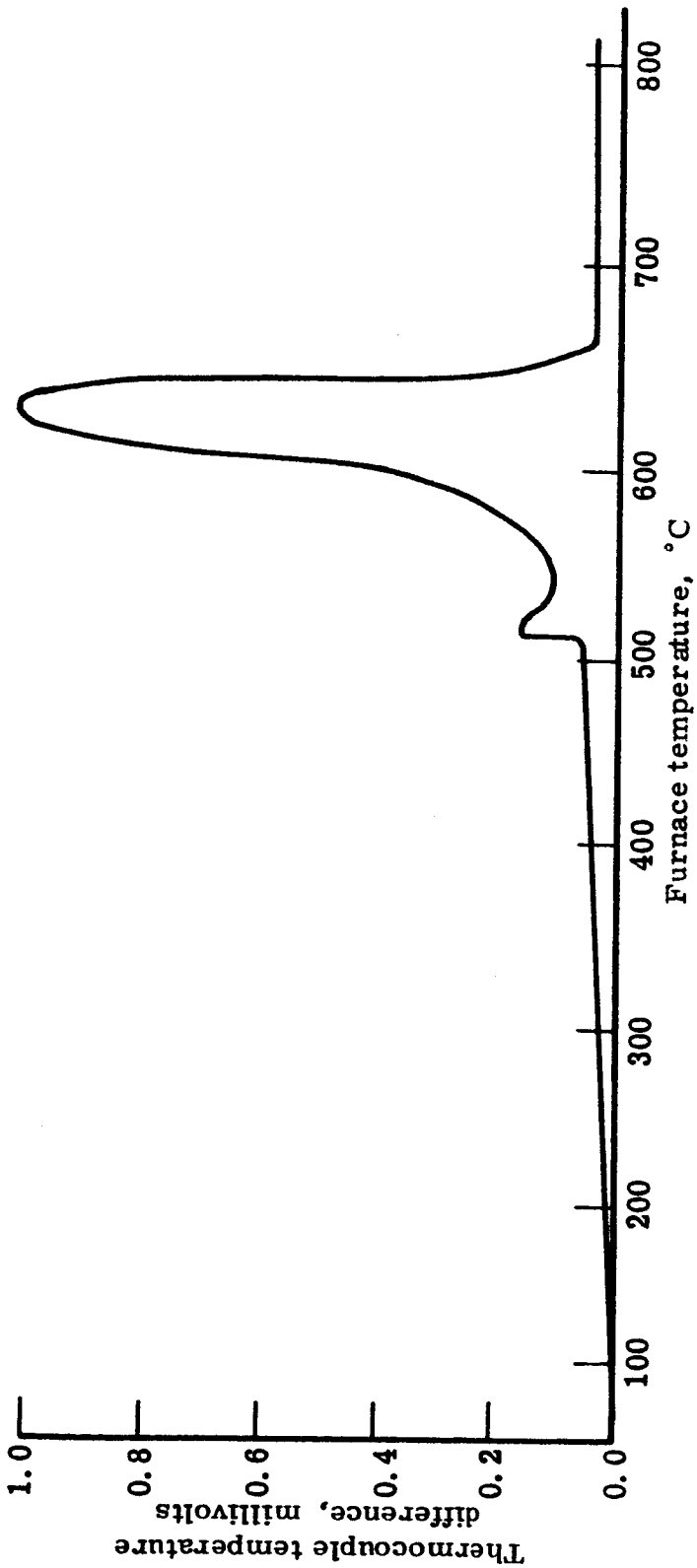


Figure 10. Differential Thermal Analysis of Polymer Made from Methylphenyl Methylamino Silazane and p,p'-Biphenol [Section VI, B.1.a.(4)]

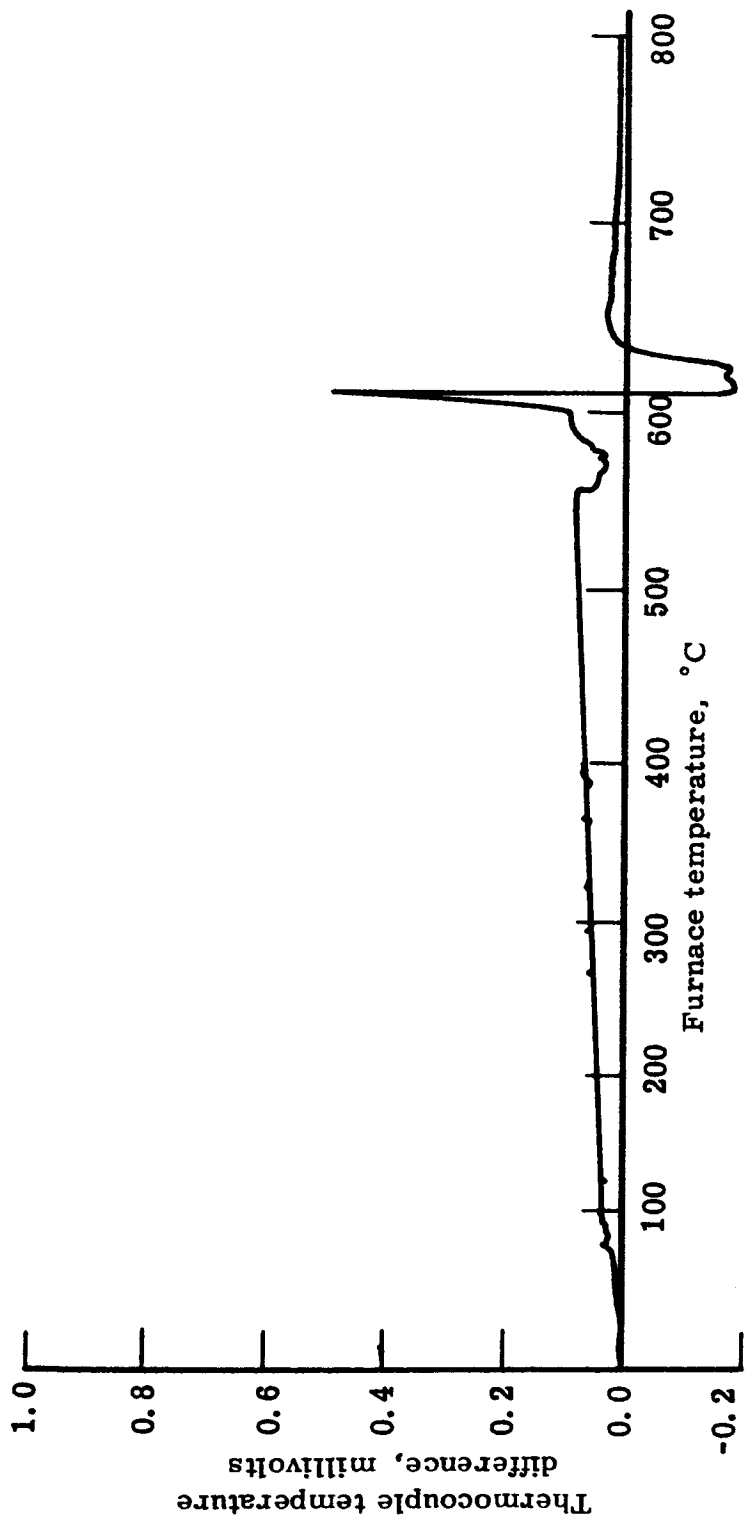


Figure 11. Differential Thermal Analysis of Polybenzimidazole.

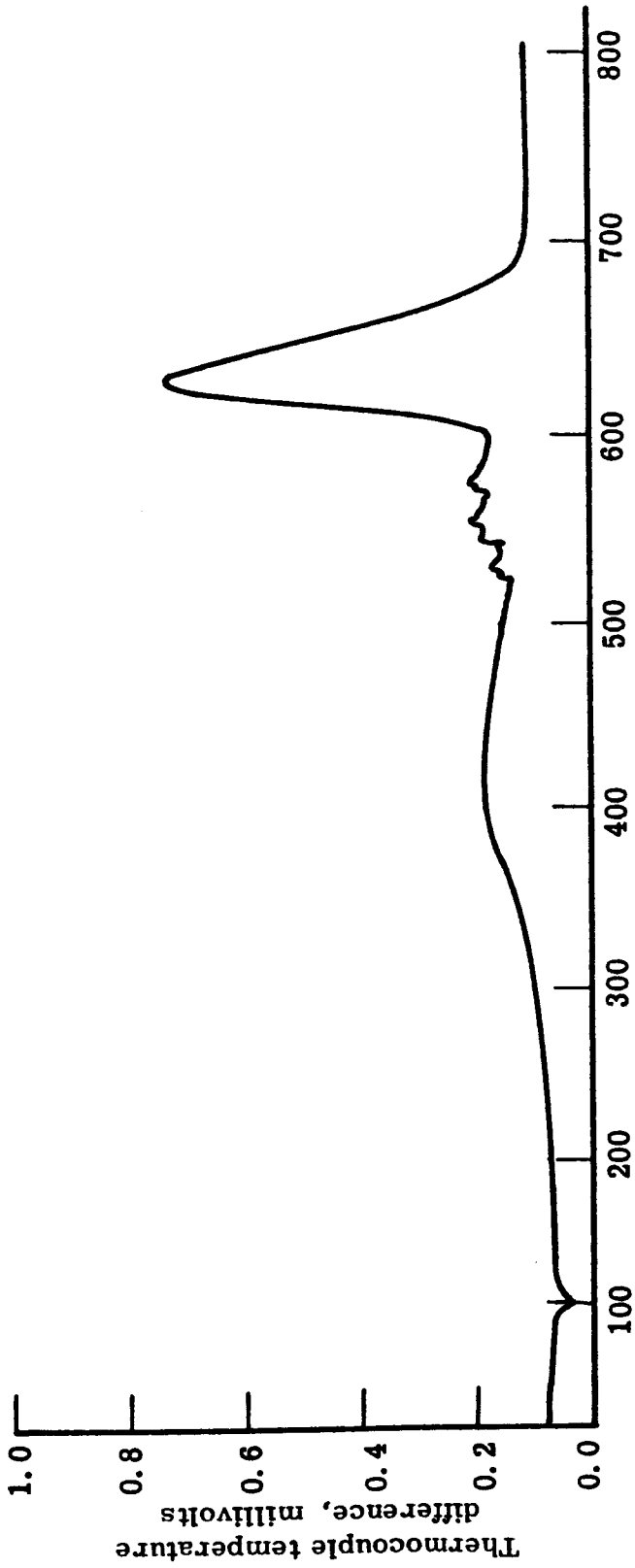
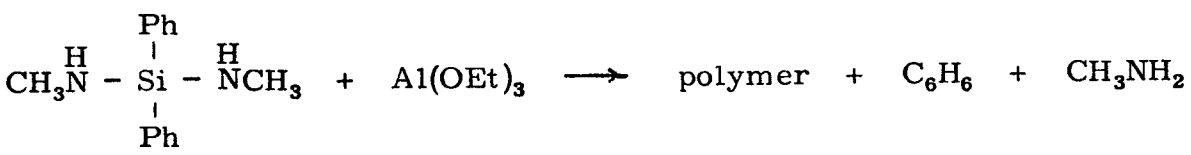


Figure 12. Differential Thermal Analysis of Phenylene-Bridged Polymer.

XII. REACTIONS OF SILYLAMINES WITH ALUMINUM ETHOXIDE, MAGNESIUM ETHOXIDE, AND ALUMINUM HYDROXIDE

A. Discussion

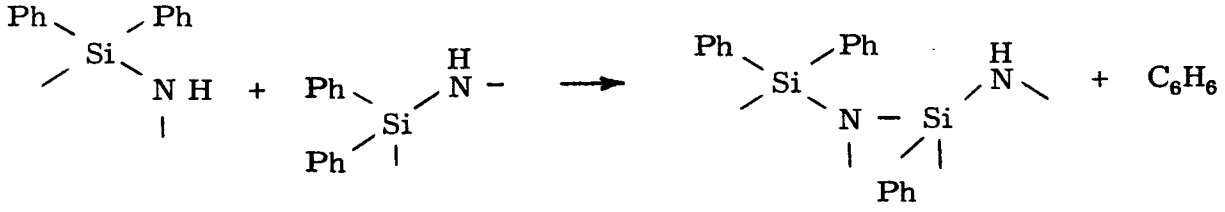
Aluminum ethoxide reacted with bis(methylamino)diphenylsilane to produce polymers of low molecular weight. The reaction was complex, and a variety of products distilled off at the reaction temperature, which was 200-300°C.



$$CH_3N(H)-Si(Ph)_2-N(H)CH_3 + Al(OEt)_3 \longrightarrow \text{polymer} + C_6H_6 + CH_3NH_2$$

$$+ CH_3NHC_2H_5 + \text{other amines}$$

The production of benzene in the reaction might be similar to the self-condensation of hexaphenylcyclotrisilazane at 450-550°C:



However, benzene was evolved from the reaction of bis(methylamino)-diphenylsilane and aluminum ethoxide at a much lower temperature.

The polymers obtained from the reactions of bis(methylamino)-diphenylsilane with aluminum ethoxide were brittle, solvent-soluble solids. When the reactants were held long enough at 300°C, the product was infusible although it was still soluble in benzene and other organic solvents. The products underwent no visible change on standing in air, and they hydrolyzed so slowly in dilute acid that it was not practical to determine their neutral equivalents. The thermal stability of the products appeared to be good in that they did not undergo gross visible decomposition at 400-500°C, but they cracked badly. Evidently the products all had low molecular weights. Furthermore, some aluminum ethoxide, or products derived from it, remained in the polymer matrix and may have continued to react further, thereby preventing attainment of a stable state.

The volatile products were analyzed in an experiment in which equivalent quantities of aluminum ethoxide and bis(methylamino)diphenylsilane were used. The reaction mixture was heated long enough to become infusible, and the solid polymer amounted to 56% of the starting material. The amount of volatile product that was condensed in a dry-ice trap was 32% of the weight of starting material. It consisted of methylamine, 40%; benzene, 32%; and at least 8 other compounds including several amines. Part of the volatile product (12% of the charge) was not condensed.

Polymerization occurred when 1, 10, or 100% of the stoichiometric quantity of aluminum ethoxide was used. The reactions were faster with larger ratios of ethoxide, but the products were all similar.

Aluminum ethoxide also reacted with hexaphenylcyclotrisilazane, but the reaction was so slow when 10% of the equivalent amount of aluminum ethoxide was used that no significant amount of polymer was produced in 7 hours at 300-360°C. Polymerization occurred when an equivalent amount of aluminum ethoxide was used, but the polymer was brittle, and no useful properties were observed.

An attempt was made to carry out a reaction between bis(methylamino)diphenylsilane and magnesium ethoxide. When equivalent quantities were used, the reaction mixture never became homogeneous, even though it was held at more than 300°C for 3.5 hours. When 10% of the equivalent amount of magnesium ethoxide was used, the product was an oil. If a reaction occurred, it did not seem promising for preparing useful polymers.

Aluminum hydroxide reacted with both bis(methylamino)diphenylsilane and hexaphenylcyclotrisilazane. It was expected that the products would be highly cross-linked, and it was hoped that the reaction might be used to produce a tough aluminum-oxygen-silicon polymer for use in glass-fiber laminates for structural materials. However, the products were all brittle. The high degree of association of aluminum hydroxide molecules with each other was probably one obstacle to a satisfactory polymerization.

B. Experimental Details

1. Reactions with equivalent quantities of aluminum ethoxide and bis-(methylamino)diphenylsilane

In a first reaction, equivalent quantities of aluminum ethoxide (2.24 g, 0.0138 mole) and bis(methylamino)diphenylsilane (4.99 g, 0.0206 mole) were placed in a 25-ml, 3-neck, round-bottom flask fitted with a reflux condenser and a thermometer. The mixture was heated until it began to evolve gas at about 200°C, even though the boiling point of bis(methylamino)diphenylsilane is about 350°C (judging from its boiling point at 1 mm). The odor of amine was strong. The evolution of gas became slower as the temperature rose to 260°C in 1.5 hour, and a low-boiling liquid began to reflux. At the end of 2 hours, the vapors were drawn off by inserting a tube from an aspirator. The appearance of the bubbles in the melt indicated that the viscosity was high, and so the reaction was stopped. As the melt cooled and solidified, bubbles were entrapped to form a yellow, foamed mass. The solid portion was clear when viewed under a microscope. The mass was soluble in benzene, acetone, and chloroform; but it was insoluble in carbon tetrachloride. After remaining at room temperature for 30 minutes, it could not be remelted. A solution of the polymer in benzene dried on a watch glass to form a hard, brittle, crazed film. It did not lose its transparency while exposed to air in the laboratory two days. A sample was examined periodically under a microscope for a week, and no evidence of evaporation or attack by moisture was seen.

A second reaction was run to obtain a product for analysis. Air was excluded by blowing the volatile liquid product away periodically with a nitrogen stream. Polymerization was stopped before the infusible state was reached. The product was pale yellow, brittle, and vitreous. Elemental analysis gave the following results:

Found: Carbon, 58.19%; hydrogen, 5.96%; nitrogen, 3.0%

Calculated for total reactants: Carbon, 59.37%; hydrogen, 8.22%; nitrogen, 6.96%; aluminum, 6.65%; oxygen, 11.84%; silicon, 6.96%.

Molecular weight (by vapor osmometry): 1120.

In a similar reaction, polymerization was allowed to proceed until the melt solidified to an infusible foamed mass. Analysis of the infusible polymer and comparison with the analysis of the fusible polymer showed that carbon and hydrogen were lost faster than nitrogen in the period immediately before the infusible state was reached. Probably the production of benzene occurred predominantly in the later stages of the reaction.

Found: Carbon, 51.50%; hydrogen, 4.04%; nitrogen, 3.3%; aluminum, 9.8%; silicon, 13.2%; remainder, 18.16%.

In an attempt to determine whether aluminum ethoxide was present in an uncombined state, the polymer was dissolved in acetone. It dissolved readily whereas aluminum ethoxide dissolves in acetone very slowly. When water was added to the acetone solution of the polymer, a precipitate formed that did not have the appearance of an aluminum hydroxide floc. Furthermore, the precipitate was soluble in an excess of acetone, and so it appeared that the aluminum had become part of the polymer.

In an attempt to determine its neutral equivalent, a sample of the polymer was dissolved in acetone, and water was added until the precipitate that formed at the point of addition just barely redissolved on stirring. Then 0.1 N acid was added. The needle of the meter used to determine the pH drifted slowly, and it was finally decided that hydrolysis was too slow for determination of the neutral equivalent by this method.

The polymer was not visibly affected by being stirred in 10% hydrochloric acid for 15 minutes at room temperature. However, it dissolved in 30 minutes at 95°C.

A fourth reaction was run for the primary purpose of trapping and identifying the volatile products. It was run in a distillation apparatus with a receiver cooled by dry ice. Aluminum ethoxide, 2.2162 g (0.0137 mole) and bis(methylamino)diphenylsilane, 4.7558 g (0.0197 mole) were heated in a 25-ml distilling flask until gas was evolved. The distillate and evolved gas were passed into a condenser-receiver combination cooled by dry ice. After 3.5 hours of gentle boiling, a slow nitrogen stream was introduced to sweep the volatile product into the receiver. After 0.75 hour of additional heating the melt became viscous and solidified while foaming. The weight of solid product was 3.8839 g (55.7% of the starting material). The distillate weighed approximately 2.2168 g (31.8% of the starting material). In addition, there was 0.0301 g (0.4%) of a high-boiling liquid in the tube between the still and the condenser receiver. The total material accounted for was 88% of the starting material. The uncondensed gas was basic in character. However, the chromatographic results described below suggest that a large part of the uncondensed product may have been hydrocarbons.

Gas chromatography of the condensed product revealed that at least 10 compounds were present as shown in Table VI. Six were basic and four were not. Methylamine (40%) and benzene (32%) were major components. The amounts of methylethylamine and xylene suggested that disproportionation was extensive. The absence of large amounts of ethanol in the product is interesting. It is possible that ethanol is produced but that it reacts as soon as it is formed to break a silicon-nitrogen bond. In that case, it may be a chain stopper.

Another reaction of this type was run in tetralin. Tetralin was chosen as the solvent because it is high-boiling and inert. Equivalent quantities of aluminum ethoxide and bis(methylamino)diphenylsilane, 7.23 g total, were dissolved in 25 ml of dry tetralin and refluxed for 12.5 hours. The tetralin was distilled off at reduced pressure, and a brown, cloudy liquid product was left. It was only partially soluble in benzene and acetone. Centrifugation of the benzene solution separated a gel-like mass. The clear benzene solution was evaporated in a stream of nitrogen, and another gel was obtained. Evidently the reaction in tetralin was different from the reaction without solvent, but no advantage was apparent.

Table VI. Chromatographic Analysis of Product from Reaction of Aluminum Ethoxide and Bis(methylamino)diphenylsilane

Fraction	TR[a]	Area, %[b]	Identity[c]
1	0.1	trace[d]	
2	0.2	1[d]	
3	0.3	2	tetramethylsilane
4	0.4	1[d]	
5	0.6	5[d]	
6	0.8	40[d]	methylamine
7	1.0	32	benzene
8	1.7	15[d]	methylethylamine
9	2.6	4	xylene
10	10.0	1	ethanol

[a] Retention time, relative to benzene = 1.

[b] Area % is essentially the same as mole percent.

[c] The tetramethylsilane is questionable; the others are reliable.

[d] These were found to be basic compounds as determined by disappearance when the sample was acidified.

The products of the reaction between aluminum ethoxide and bis(methylamino)diphenylsilane, without solvent, were tried as coating agents, but they were not promising. When thin films were heated on aluminum panels at 300°C for 16 hours they flaked off, or were easily scratched off with a fingernail.

2. Reaction of bis(methylamino)diphenylsilane with 10% of the equivalent quantity of aluminum ethoxide

In an attempt to determine whether the role of aluminum ethoxide in the reaction with bis(methylamino)diphenylsilane was catalytic, a reaction was run with 10% of the stoichiometric amount. In a 25-ml, 3-neck flask were placed 4.99 g (0.0206 mole) of bis(methylamino)diphenylsilane and 0.22 g (0.0014 mole) of aluminum ethoxide. The mixture was heated until gas evolution started. After 1.75 hours of heating, condensate began to form in the condenser. When sputtering became excessive as the condensate fell into the melt, nitrogen was used to blow the condensate out. At the end of 3 hours (total) the reaction was stopped. The product was a pale yellow, brittle, vitreous solid that softened in a capillary tube at 67-71°C. On the next day, heating was resumed for 6.5 hours. The softening point of the final solid product, 3.3 g, was 114-122°C. Elemental analysis gave the following results:

Found: Carbon, 65.74%; hydrogen, 5.50%; nitrogen, 7.39%; aluminum, 2.8%; silicon, 13.4%; remainder, 5.17%.

Calculated for total reactants: Carbon, 67.77%; hydrogen, 7.60%; nitrogen, 10.87%; aluminum, 1.04%; oxygen, 1.85%; silicon, 10.87%.

Nuclear magnetic resonance spectra indicated that the ratio of phenyl to methyl groups in the product was 1.5 : 1; no ethyl and no NH groups could be detected.

For comparison, bis(methylamino)diphenylsilane, alone, was boiled gently for 3 hours. Gas evolution was comparatively slow throughout the period. When cool, the product was a mixture of solid and crystalline material. There seemed to be no doubt that aluminum ethoxide accelerated the reaction.

A similar reaction, with 10% of the stoichiometric amount of aluminum ethoxide, was performed in a long open-end glass tube in an oven at 300°C for 22 hours. The product was a brown polymer that softened at 82-98°C. It appeared to be similar to the other polymers of this type in brittleness, solubility, and softening point, and so no further work was done on it.

3. Reaction with 1% of the equivalent quantity of aluminum ethoxide

The aluminum ethoxide-bis(methylamino)diphenylsilane reaction was run with only 1% of the stoichiometric amount of aluminum ethoxide. After 4.75 hours of heating at a temperature adjusted to keep gas evolving slowly (257-346°C as the reaction progressed) a viscous liquid was produced. The liquid solidified on cooling; the softening point was 97-117°C. The product resembled the others obtained from reactions with larger ratios of aluminum ethoxide in solubility and behavior on heating.

4. Attempted reactions with ethanol and phenol

To check the possibility that ethanol might be produced and act as the sole catalytic agent in the reaction of bis(methylamino)diphenylsilane and aluminum ethoxide, bis(methylamino)diphenylsilane was treated with 10% of the stoichiometric amount of ethanol in one experiment, and with 10% of the stoichiometric amount of phenol in another. No aluminum ethoxide was present in either. After being refluxed for 3 hours and left overnight at room temperature, neither reaction yielded a solid product. The phenol and ethanol reactions did not resemble any of the aluminum ethoxide reactions closely nor were they entirely like that which occurred on simple heating of bis(methylamino)diphenylsilane. It is clear that the aluminum ethoxide reaction is not simply a matter of forming ethanol by hydrogen exchange, followed by attack of ethanol on silicon-nitrogen bonds.

5. Attempted reactions between aluminum ethoxide and hexaphenylcyclotrisilazane

a. 10% aluminum ethoxide

Hexaphenylcyclotrisilazane, 8.17 g (0.0138 mole), and aluminum ethoxide, 0.22 g (0.0014 mole), were heated together in a 50-ml flask. They fused to a homogeneous melt on heating to 230°C while being stirred with a magnetic stirrer. In 2 hours, the temperature reached 290°C, and smoking and sputtering began. After 1 hour the vapors were blown out with nitrogen. Heating was continued for 5 hours more to a final temperature of 360°C. When cool, the reaction product was a friable, cloudy, tan solid that appeared to melt in a capillary tube at 209-214°C. No polymer appeared to have been formed.

b. Equivalent amounts of hexaphenylcyclotrisilazane and aluminum ethoxide

In a 50 ml, 3-neck, round-bottom flask equipped with a thermometer, reflux condenser, and magnetic stirrer were placed 8.17 g (0.0138 mole) of hexaphenylcyclotrisilazane and 2.24 g (0.0138 mole) of aluminum ethoxide. Heat was applied, and a homogeneous melt was obtained at 225°C. After 1.0 hour of heating some volatile material began to reflux while the melt was at 331°C. Periodically, the vapors were swept out with a stream of nitrogen, and after 2.5 hr of heating, the mixture formed 6.83 g of brittle, infusible, foamed polymer that was solid at 370°C. This product was soluble in benzene, but attempts to prepare coatings with it on aluminum were not successful, because the polymer turned white and flaked off.

6. Reaction of bis(methylamino)diphenylsilane with magnesium ethoxide

Magnesium ethoxide was prepared by the method of Cohen.[30] In a first reaction, equivalent amounts of bis(methylamino)diphenylsilane, 4.99 g (0.0206 mole), and magnesium ethoxide, 2.36 g (0.0206 mole) were weighed in a nitrogen atmosphere and placed in a 25-ml, round-bottom, 3-neck flask. The temperature was increased to 290°C over a 2-hour period while methylamine was evolved slowly. After 2.75 hours of additional heating, the mixture was tan and the temperature was 320°C. After 3.5 hours of additional heating the product was semi-solid. On cooling, it was a brittle semi-solid, that was partially soluble in benzene.

In a second reaction, the temperature was not allowed to go above 275°C. After 6.5 hours, the product was a gray slurry at 275°C and at room temperature.

In a third reaction, 10% of the equivalent amount of magnesium ethoxide was used. After 10 hours of heating at 220-240°C the product was a tan, viscous, liquid. Evidently magnesium ethoxide did not react in the same manner as aluminum ethoxide.

7. Reaction of bis(methylamino)diphenylsilane with aluminum hydroxide

Several exploratory reactions were run in which varying amounts of aluminum hydroxide and bis(methylamino)diphenylsilane were heated together. They reacted with the evolution of methylamine and the formation of friable solids. Grinding the solids and heating them with additional bis(methylamino)diphenylsilane failed to produce any products that appeared to be polymers.

In a reaction with equivalent quantities of the two reactants [3 moles of bis(methylamino)diphenylsilane to 2 moles of aluminum hydroxide], the reaction mix bubbled gently when heated to 150°C. In 1 hour, when the temperature had reached 190°C, refluxing began. Evidently a condensable liquid, probably benzene was being formed. After another 2 hours, when the temperature reached 350°C, the mixture was quite fluid, and it contained an undissolved white solid. The melt became a brittle white solid when cooled to room temperature. Further heating at 175°C for 16 hours produced no significant change.

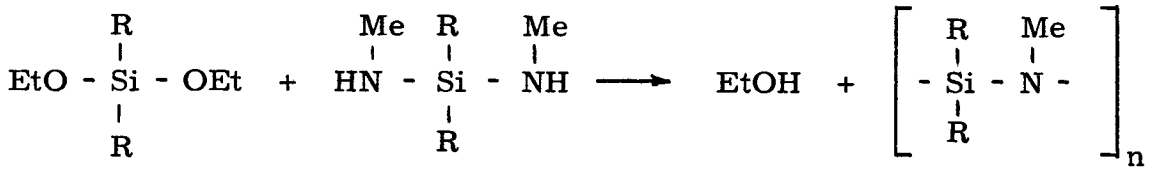
8. Reaction of hexaphenylcyclotrisilazane with aluminum hydroxide

Equivalent quantities of hexaphenylcyclotrisilazane and aluminum hydroxide were mixed and gradually heated to 235°C in 1.5 hour, at which point foaming began. On further heating to 310°C in 1 hour, a small amount of low-boiling material formed. Heating was continued for 2.75 hours. When cooled, the product was a white, brittle solid. Further heating in air at 175°C for 22.5 hours and 250°C for 7 hours produced a liquid that solidified when cooled below 180°C to a friable mass that was partially soluble in benzene. Evidently no significant amount of polymerization occurred.

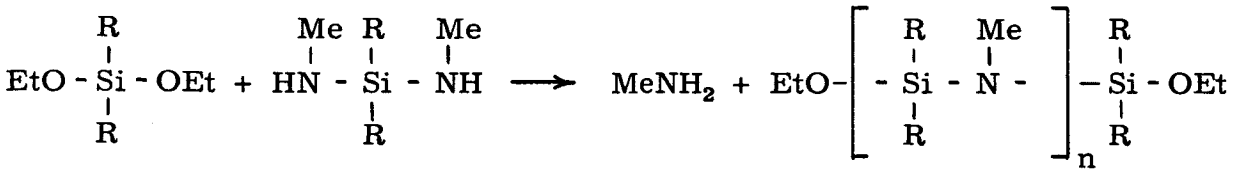
XIII. ATTEMPTS TO PROMOTE REACTION BETWEEN ETHOXYSILANES AND AMINOSILANES

A. Discussion

If ethoxysilanes and aminosilanes could be made to react with the elimination of either amines or alcohols, the reaction could probably provide a useful route to polymers, and the reaction would have an advantage over the ammonia-chlorosilane reaction in not forming hydrochloric acid as a by-product.



Any ethanol produced would be likely to react with Si-NHMe groups to release methylamine and produce a new Si-OEt group, which could then react with additional Si-NHMe groups. The net result would be this, with the ethoxy groups being required in relatively small amounts:



Bis(methylamino)diphenylsilane and dimethyldiethoxysilane were heated together under three different sets of conditions at atmospheric pressure: the two alone, the two with a catalytic amount of ammonium chloride, and the two with a catalytic amount of diphenyldichlorosilane. There was no evidence in any of these trials that the two compounds polymerized to a significant extent. Higher pressures and temperatures were also tried, but again no appreciable reaction was detected.

When aluminum ethoxide was tried as a catalyst in a reaction between bis(methylamino)diphenylsilane and diphenyldiethoxysilane, a brittle, transparent solid that softened at 75°C was obtained.

Potassium was tried as a catalyst in reactions of diphenyldiethoxysilane with bis(methylamino)diphenylsilane and with hexamethylcyclotrisilazane. The reactions were evidently complex, and some gels were obtained. The gels became friable powders when heated. No polymers with desirable physical properties were isolated.

B. Experimental Details

1. Reaction between bis(methylamino)diphenylsilane and dimethyldiethoxysilane at atmospheric pressure

a. Without catalyst

Bis(methylamino)diphenylsilane (1.62 g, 0.007 mole) and dimethyldiethoxysilane (1.00 g, 0.007 mole) were refluxed for 10 hours. The temperature of the mixture rose gradually from 121 to 138°C. The product was a cloudy, viscous liquid. Evidently a small amount of polymerization occurred, but it could have been a result of self-condensation of bis(methylamino)diphenylsilane. Since a much higher degree of polymerization was required for the reaction to be useful, two experiments with acidic materials were tried as described below.

b. With ammonium chloride

Bis(methylamino)diphenylsilane (10.0 g, 0.041 mole) and dimethyldiethoxysilane (6.08 g, 0.041 mole) were mixed and refluxed for 15.5 hours; the product was still liquid. Then 0.34 g (0.006 mole) of ammonium chloride was added, and refluxing was continued. A strong odor of amine was noticed after the ammonium chloride was added. After 5 hours of refluxing with the ammonium chloride, the reaction was terminated and 4.0 g of volatile material was distilled off at atmospheric pressure. The index of refraction of the distillate was n_D^{26} 1.3790, which is close to that of dimethyldiethoxysilane, n_D^{26} 1.3798, and different from that of ethyl alcohol, n_D^{26} 1.3590. The residue was a viscous liquid. Consequently, it was concluded that there had been little or no reaction.

c. With diphenyldichlorosilane

Bis(methylamino)diphenylsilane (5.0 g, 0.0206 mole), dimethyldiethoxysilane (3.04 g, 0.0206 mole), and diphenyldichlorosilane (0.16 g, 0.0006 mole) were refluxed for 9 hours. No evolution of gas or increase in viscosity was apparent. A small amount, 1.8 g, of volatile material was distilled off; and a soft, solid residue was obtained. Again the amount of polymerization that occurred was insufficient to be of interest.

d. With aluminum ethoxide (10%)

In a 20-ml, 2-neck, round-bottom flask equipped with a reflux condenser, thermometer, and boiling chip were placed 4.6 ml (5.0 g 0.0206 mole) of bis(methylamino)diphenylsilane, 3.6 ml (3.04 g, 0.0206 mole) of dimethyldiethoxysilane, and 0.22 g (0.0013 mole) of aluminum ethoxide. Heat was applied, and a homogeneous solution formed in 30 minutes when the temperature reached 135°C. After 5.75 hours of heating, the temperature had risen to 160°C, but there was no visible evidence that any reaction had occurred. Heating was continued for a total of 18.25 hours, the final temperature being 188°C. There was no change in appearance or viscosity of the solution. About 2.0 ml (1.82 g) of liquid was distilled at 135°C. Evidently, little or no reaction occurred.

2. Reaction between bis(methylamino)diphenylsilane and dimethyldiethoxysilane under pressure

It was expected that a higher temperature would afford a better chance of reaction with bis(methylamino)diphenylsilane. Consequently, two reactions were attempted in steel bombs to permit the use of temperatures above the boiling point of dimethyldiethoxysilane, which is 113°C.

In the first reaction, 0.13 g (0.0009 mole) of dimethyldiethoxysilane and 2.32 g (0.0096 mole) of bis(methylamino)diphenylsilane were heated in a 43-ml stainless-steel bomb at 190°C for 17.5 hours. The product had the same appearance as the starting materials with no evidence of polymerization. A second reaction was tried with the same procedure and quantities, except with the addition of 3.97 g of triethylamine. When the triethylamine was distilled from the product, the residue was a cloudy, yellow liquid that evidently had not polymerized appreciably.

3. Reactions between bis(methylamino)diphenylsilane and diphenyldiethoxysilane

a. With aluminum ethoxide

In a 25-ml, 3-neck, round-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser were placed 4.6 ml (5.0 g, 0.0206 mole) of bis(methylamino)diphenylsilane, 5.4 ml (5.61 g, 0.0206 mole) of diphenyldiethoxysilane, and 0.22 g (0.0013 mole) of aluminum ethoxide, which is 10% of the equivalent amount. Heat was applied, and a homogeneous solution formed when the temperature reached 145°C. About 10 minutes later, at 190°C, the solution began to turn gray. Refluxing began at 299°C, and after 1.25 hour of heating the condensate began to smoke and sputter as it dripped back into the reaction mixture. The vapors were swept out periodically with a stream of nitrogen. Heating was continued, and after 5.75 hours, with the temperature at 360°C, the solution was a dark gray liquid. The product, after cooling overnight, was a gray, tacky, transparent, vitreous solid that weighed 5.67 g and that melted at 75-84°C. It was applied to an aluminum panel from a benzene solution; after curing, it formed a brittle coating that could be scraped from the panel with a fingernail.

A similar reaction was run with the same amounts of material but without the aluminum ethoxide. After 13.25 hours of refluxing at 315-322°C, the product was 9.48 g of a mixture of white solid and grayish-tan liquid. Evidently the aluminum ethoxide was necessary to obtain the polymer.

b. With potassium

Potassium was tried as a catalyst for the reaction of bis(methylamino)diphenylsilane and diphenyldiethoxysilane. In a 100-ml, 3-neck, round-bottom flask were placed 20 ml of dry purified dioxane and 1.77 g (0.0453 mole, 10% excess) of potassium. This was heated to 65°C with stirring to disperse the potassium. Then 4.99 g (0.0206 mole) of bis(methylamino)diphenylsilane in 15 ml of dioxane was added through the dropping funnel. The solution immediately became dark red; and, in about 5 minutes, it became viscous and a large amount of white solid appeared. In 2 hours of refluxing the liquid became tan, and the solid remained. The mixture was cooled to room temperature, and 5.4 mole (5.61 g, 0.0206 mole) of diphenyldiethoxysilane in 10 ml of dioxane was added. The temperature was increased to 60°C, and the color became darker as the viscosity decreased. Two hours at 100°C produced no additional change except further darkening. After standing overnight the mixture was centrifuged to separate a gel and a thin dark liquid. The gel became powdery but did not melt when heated strongly. The dark liquid yielded a soft, black solid when the solvent was removed.

4. Reaction between the potassium derivatives of hexamethylcyclotrisilazane and diphenyldiethoxysilane

In a 100-ml, 3-neck, round-bottom flask were placed 40 ml of dry purified dioxane and 1.72 g (0.044 mole, 10% excess) of potassium. This mixture was heated to 65°C with stirring to disperse the potassium. Then 4.61 ml (4.39 g, 0.020 mole) of hexamethylcyclotrisilazane in 10 ml of dry dioxane was added. This mixture was refluxed at 101°C for 11.75 hours. At the end of this time, some of the potassium had not reacted. The mixture was cooled to room temperature, and 5.24 mole (5.45 g, 0.020 mole) of diphenyldiethoxysilane in 10 ml of dioxane was added. During 1.5 hour of additional refluxing, most of the metallic potassium disappeared, but some still remained after 10.5 hours. The reaction mixture contained both solid and liquid at this time. Centrifugation separated a gel and a liquid. The gel became a friable powder when heated. The solution yielded 8.41 g of a sticky, semi-solid mass when the solvent was removed. This semi-solid mass had no apparent desirable qualities. It had no promising coating properties.

XIV. POLYMERIZATION OF HEXAPHENYLCYCLOTRISILAZANE IN SEALED VESSELS AT HIGH TEMPERATURE

Groszos and Hall[31] stated that hexaphenylcyclotrisilazane could be polymerized in sealed vessels at temperatures up to 700°C to produce thermoplastic polymers. Trials were made to determine whether the polymer obtained by their method differed significantly from the polymer that we have produced by heating in air.

Hexaphenylcyclotrisilazane, 1.97 g, was placed in a 45-ml, stainless steel bomb and heated at 600°C for 10 minutes. The bomb was cooled and opened, and the product was a brown, brittle solid. It was soluble in benzene and had a melting range of 173-202°C. Evidently this was a satisfactory example of their product. It was suspected of being very much like the prepolymer that we have often made from hexaphenylcyclotrisilazane, because it performed almost identically when made into coatings on aluminum in that it was stable but brittle. To confirm the similarity further, a prepolymer was made by our method by boiling hexaphenylcyclotrisilazane in a test tube at atmospheric pressure until it appeared to be about to solidify. After being cooled, pulverized, and placed in a capillary tube, it melted at 195-216°C.

The intrinsic viscosities of both products showed that they both had low molecular weights, that of the prepolymer being slightly higher. In previous work,[32] the highest molecular weight determined for a prepolymer made by heating hexaphenylcyclotrisilazane was 1400. There seems to be no advantage in studying the Groszos and Hall method further.

XV. REACTIONS OF ETHYLENEDIAMINE SILAZANE

A. Discussion

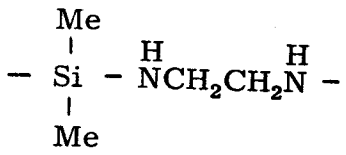
Ethylenediamine silazane (EDS) has been used previously in this research program to form resilient polymers with good thermal and chemical stability, but they have had poor strength. Attempts have been made at various times to improve the strength, but no significant improvement has been accomplished. EDS has been used in combination with other materials to improve their flexibility and thus provide better properties in coatings and resilient plastics. During the period covered by this report, attempts have been made to improve EDS by treating it with epoxy compounds, bis(methylamino)diphenylsilane, hydroquinone, and silicon tetrafluoride.

The treatment of EDS with bis(methylamino)diphenylsilane seems to have resulted in a worthwhile improvement in the ability of EDS to combine with the by-product of hexaphenylcyclotrisilazane to form coatings. Inasmuch as coatings made with EDS and the by-product have considerable potential utility, this could be an important development.

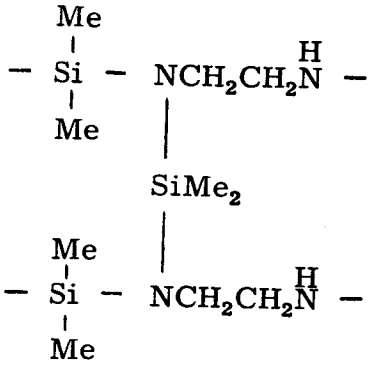
Reactions of EDS with small amounts of ethylene oxide, hydroquinone, Epon 828 (an epoxide starting material for epoxy polymers), and silicon tetrafluoride were disappointing. Although some reaction occurred between EDS and the epoxides, coatings made from the products were not homogeneous, and no promising leads to useful materials were found. When EDS was treated with silicon tetrafluoride, moisture-sensitive liquids, gels, and powders were formed. Treatment of EDS with hydroquinone led to a polymer that was slow in curing and that was brittle when cured.

Addition of triethylamine in a preparation of EDS seemed to increase the toughness of films subsequently prepared from the product to a slight degree.

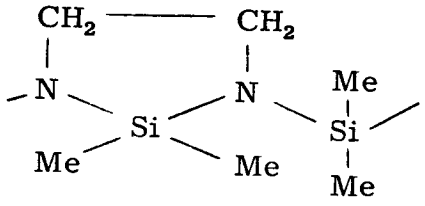
The term "ethylenediamine silazane" has been used in this program for the liquid polymer made by the reaction of dimethyldichlorosilane with ethylenediamine. The lack of specificity in the term is appropriate because the polymer is probably a mixture of linear, cross-linked linear, cyclic, and ladder forms, such as the following:



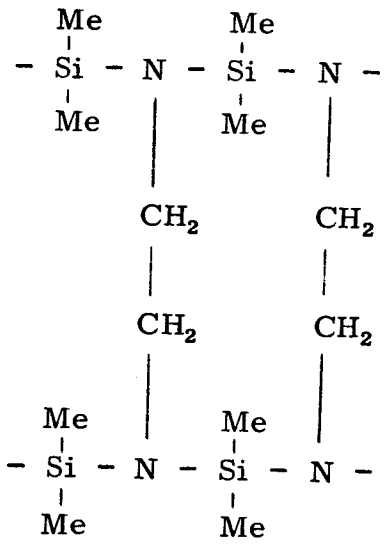
linear form



cross-linked linear form



cyclic form



ladder form

The linear and the cross-linked linear forms offer opportunities for additional cross-linking or chain extension, and it was this possibility that led to the attempted reactions with bis(methylamino)diphenylsilane and the epoxides.

B. Experimental Details

1. Reaction of EDS with bis(methylamino)diphenylsilane

The exact amount of replaceable hydrogen in EDS was not known, and so an empirical method of calculating equivalence based on silicon contents was adopted. The approximate amount of silicon in EDS was known by analysis,[33] and the amount of silicon in bis(methylamino)diphenylsilane was known from its formula.

a. Reaction with 25% of the equivalent quantity of bis(methylamino)diphenylsilane

EDS was made by the reaction of dimethyldichlorosilane with ethylenediamine as received from Union Carbide Chemicals Company.[33] EDS, 5.14 g (0.054 g atoms of silicon), and bis(methylamino)diphenylsilane, 4.31 g (0.014 g atoms of silicon), were stirred and heated together at 250°C for 8 hours in a flask fitted with a thermometer, a reflux condenser, and a drying tube. A gas was evolved that smelled like an amine, and the color of the reaction mixture darkened slightly, but no visible change in viscosity occurred. The product was a light brown, viscous liquid. When the product (dissolved in benzene) was applied to an aluminum panel and heated at 190°C for 5 hours, it formed a fairly tough coating, but it could be scratched with a fingernail. It appeared to be slightly tougher and showed less tendency to wrinkle in the thick portions than a coating made with the original EDS.

b. Reaction with 7% of the equivalent quantity of bis(methylamino)diphenylsilane

EDS, 10.4 g (0.125 g atoms of silicon) and bis(methylamino)-diphenylsilane, 2.17 g (0.009 g atoms of silicon), were stirred and heated together at 250°C for 8 hours in a 25-ml flask fitted with a reflux condenser and drying tube. Amine was evolved, and the color darkened. The product was a dark brown, viscous liquid, and coatings made from it were essentially the same as those described in the preceding paragraph.

c. Coatings made with modified EDS and the hexaphenylcyclotrisilazane by-product

Coatings were made from a mixture of EDS modified as described in the preceding paragraph and the by-product obtained in the preparation of hexaphenylcyclotrisilazane.[5] The by-product, 9 parts, and the modified EDS, 1 part, were dissolved in benzene to form a 10% solution. The solution was spread on aluminum, the benzene was evaporated, and the residual film was heated at 190°C for 45 hours. The coating produced was shiny, transparent, and hard. The coating protected the aluminum from 19% hydrochloric acid even when it had been bent after heating. A similar coating made with unmodified EDS and the by-product cracked at the bend.

2. Reaction of EDS with ethylene oxide

EDS, 11.6 g (0.122 g atoms of silicon), was dissolved in 100 g of anhydrous benzene in a 200-ml, round-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser. The solution was cooled to 7°C in an ice bath, and liquid ethylene oxide, 0.48 g (0.011 mole), was added. The solution was stirred at 7°C for 30 minutes, and then it was allowed to warm to room temperature over a period of an hour. The solution was refluxed at 78°C for 2 hours, and then the benzene was distilled off. The product, 11.9 g, was a brownish-yellow, viscous liquid. Coatings made with the product were essentially the same as those made with EDS.

Another reaction was tried with gaseous ethylene oxide. EDS, 11.7 g, was dissolved in 50 ml of anhydrous benzene, and the vapor from 60 ml of liquid ethylene oxide was passed over the surface of the benzene solution as it was being stirred. The temperature rose from 24°C to 35°C in 10 minutes and then fell gradually back to 27°C. The reaction mixture was stirred for 4 hours as the ethylene oxide was being added, and then it was refluxed for 4.5 hours. During refluxing, the temperature of the solution was 29°C, indicating that an excess of ethylene oxide was present. After the solution had stood at room temperature for 3 days, it was refluxed for 5 hours, during which time the temperature rose to 79°C. At the end of this period the benzene was distilled off. The product was a brownish-yellow viscous liquid that weighed 10.3 g. Coatings made with the product were soft and could be scratched easily. They appeared to be essentially the same as those made with EDS.

3. The reaction of EDS with Epon 828

a. Reaction of EDS with 1% by weight of Epon 828

EDS, 9.9 g (0.101 g atoms of silicon), and Epon 828, 0.1 g, obtained from Shell Chemical Company were mixed in a 25-ml, round-bottom flask equipped with a thermometer, magnetic stirrer, and reflux condenser. The mixture was heated slowly up to 155°C and held at this temperature for 1.0 hour. It was then heated at 210°C for 1.0 hour. The temperature was increased to 270°C in 30 minutes. The product was a dark brown semi-solid flecked with lumps of a white solid. Efforts to dissolve the white solid by heating and with solvents such as benzene, dioxane, and tetrahydrofuran were unsuccessful. The preparation of coatings was not attempted because of the non-homogeneity of the product.

b. Reaction of EDS with 10% by weight Epon 828 in dioxane solution

EDS, 9.0 g (0.092 g atoms of silicon) was dissolved in 12.0 g of purified dioxane in a 50-ml, round-bottom flask equipped with a reflux condenser, thermometer, and magnetic stirrer. Epon 828, 1.0 g, was dissolved in 10 ml of purified dioxane and added drop-wise. The mixture was stirred for 1 hour, and then heated to 60°C for 1 hour. The dioxane was distilled off, and heat was applied until the temperature reached 310°C and the product became solid. Coatings made from the product, separated into hard and soft portions. Evidently dispersion of the Epon 828 had not been complete.

4. Reactions of EDS with hydroquinone

a. Equal weights of EDS and hydroquinone

EDS, 7.59 g (0.078 g atoms of silicon), was treated with a solution of hydroquinone, 7.48 g (0.0679 mole), in 20 ml of tetrahydrofuran in a 100-ml, round-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser. The temperature rose 16°C, and the brown solution in the flask turned white. The solution was refluxed for 2 hours at 75°C, then the tetrahydrofuran was distilled off. The temperature of the reaction product was increased gradually for 5.75 hours to a final temperature of 280°C. The product was a dark brown, sticky, viscous liquid. Coatings made with the product cracked when bent and were easily scratched with a fingernail.

b. 1% by weight of hydroquinone

Hydroquinone, 0.1 g (0.0009 mole), was dissolved in 10 ml of tetrahydrofuran and added drop-wise to EDS, 9.9 g (0.10 g atoms of silicon), dissolved in 10 ml of tetrahydrofuran in a 50-ml, round-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser. The temperature rose 11°C during addition of the hydroquinone solution. After the mixture had refluxed at 70°C for 2 hours, the tetrahydrofuran was distilled off. The temperature of the reaction product was increased gradually over 2.5 hours, from 70°C to 220°C. The product was more viscous than the original EDS resin. It was a light brown, sticky, viscous liquid. Coatings made with the product cracked when cooled and could be scratched easily.

5. Preparation of EDS in presence of triethylamine

Previous success with the use of triethylamine in the reaction of silicon halides with amines prompted a trial in the preparation of EDS.

Dimethyldichlorosilane, 64.52 g (0.5 mole), was dissolved in 750 ml of anhydrous benzene in a 2-liter, round-bottom flask, equipped with a reflux condenser, mechanical stirrer, and dropping funnel. Triethylamine, 101.2 g (1.0 mole), was added to the benzene solution drop-wise with stirring. The mixture was stirred vigorously for 4 hours, and then ethylenediamine, 150.25 g (2.5 mole), was added drop-wise while stirring was continued. The reaction mixture was refluxed at 80°C for 4 hours. Then the benzene layer was separated from the oily layer, and the benzene was removed at reduced pressure. The product was a yellow, viscous liquid. Coatings made from the product were slightly tougher than those made with EDS prepared without triethylamine, but they were quite soft and easily scratched.

6. Reaction of EDS with silicon tetrafluoride

Previous work on the addition of silicon tetrafluoride to hexamethylcyclotrisilazane produced a vitreous material of exceptional thermal stability.[34] This reaction prompted attempts to bring about a more favorable reaction with EDS.

EDS, 10.3 g (0.106 g atoms of Si), was dissolved in 100 ml of anhydrous benzene in a 300-ml, round-bottom flask equipped with a reflux condenser, a thermometer, and gas-inlet tube. A cylinder of silicon tetrafluoride was attached directly to the reaction flask with a rubber tube, and the flow of gas into the reaction flask was regulated so that it kept a balloon, attached to the top of the reflux condenser, inflated. The positive pressure of silicon tetrafluoride was maintained for 1.5 hours. For the last 0.5 hour no silicon tetrafluoride was admitted, and there was no apparent change in the size of the balloon. The weight of silicon tetrafluoride that reacted was 2.65 g (0.0254 mole).

The mixture was heated slowly; and when the temperature reached 50°C, white flakes of solid appeared in the clear solution. The temperature was increased to 80°C, and the solution was refluxed at that temperature for 3 hours. Samples removed from the flask and exposed to air turned cloudy immediately and dried to a white powdery solid. The benzene was drawn off leaving in the reaction flask a gel with flakes of crystalline solid. On heating about a gram of the product at 260°C for 1.5 hours, it turned dark black and became a very brittle solid. Thus the reaction of silicon tetrafluoride with EDS appears to be less encouraging than the reaction of silicon tetrafluoride with hexamethylcyclotrisilazane.

XVI. ATTEMPTS TO DETERMINE BOND STRENGTHS IN CYCLIC SILAZANE AND SILOXANE COMPOUNDS

A. Discussion

Attempts were made to determine strengths of silicon-nitrogen and silicon-oxygen bonds, because data in the literature do not explain the observed thermal stability of some of the silazane compounds. Calorimetric measurements of heats of combustion were attempted as a basis for calculating the silicon-oxygen and silicon-nitrogen bond strengths. The plan was to relate these bond strengths to the thermal stabilities of the siloxane and silazane compounds. However, it proved to be difficult to achieve complete combustion of the compounds in a bomb calorimeter. Evidently previous investigators have had the same trouble.

Previous investigators found that during combustion in a bomb calorimeter, a crust of silica formed and protected part of the silicon compounds. Thompson,[35] in his thermochemical analyses of siloxane compounds, used benzoic acid as a promoter and found that it did not aid combustion; but he claims to have obtained complete combustion by a different technique in which he used two soft glass ampoules that were designed to explode at different time intervals during the burning. However, he admits that construction of glass ampoules that explode at the proper time is actually a matter of chance. Tanaka, et al[36] claim to have obtained complete combustion of some siloxane compounds by using glass ampoules to hold the sample. However, the heats of combustion measured by Tanaka are not in good agreement with measurements made by other investigators. Tanaka gives no indication of having detected crust formation in any of his calorimetric tests. Very little work has been done on the silazane compounds, and, therefore, comparison of the silicon-oxygen bond strength with the silicon-nitrogen bond strength is difficult. We attempted to develop a method of obtaining complete combustion of a cyclic silazane and a cyclic siloxane compound in an oxygen bomb.

In preliminary experiments intended to find a method of obtaining complete combustion, no attempt was made to make calorimetric measurements. Samples of hexamethylcyclotrisilazane, octamethylcyclotetrasiloxane, and solutions of each of these silicon compounds in highly combustible organic solvents were weighed in gelatin capsules; and the capsules were burned in an oxygen bomb. The silica crusts formed in these experiments indicated that the liquid samples would have to be distributed in some manner so that more surface area was exposed to oxygen for burning. Several different methods of providing more surface area were tried in efforts to obtain complete combustion. The methods tried were: spreading of the liquid sample in a thin film in a stainless-steel calorimeter pan, dispersal of the liquid on an asbestos-fiber mat, and creation of small liquid droplets completely exposed to oxygen. None of these methods resulted in complete combustion of the silicon compounds. A visual inspection of the oxygen bomb after each test indicated that the formation of a silica crust had prevented portions of the sample from burning. Calorimetric measurements were not attempted because an acceptable combustion method was not found. Obviously extensive effort would be required to find a means of improving combustion, and this amount of effort is not recommended at present.

B. Experimental Details

A commercial double-valve stainless steel oxygen bomb was used for the combustion tests. The bomb was charged with oxygen to a pressure of 25 atmospheres prior to each of the combustion tests. For ignition of the sample, a 34-gage Nichrome wire, 11 cm in length, was connected between the electrodes and secured in position so that it touched the sample.

Hexamethylcyclotrisilazane and octamethylcyclotetrasiloxane were burned in the oxygen bomb as pure compounds and as mixtures with diethylether or benzene. The diethylether mixtures appeared to burn more completely than either the pure compounds or the benzene mixtures.

1. Combustion of the samples in gelatin capsules

Several samples of silazane and siloxane compounds were burned in thermally calibrated calorimeter capsules of gelatin. The gelatin capsules appeared to explode upon ignition and scatter the sample so that they aided in preventing the formation of a crust of silica. The crust that formed during the burning usually was in the form of thin flakes, and it was gray in color or speckled with black.

Hexamethylcyclotrisilazane, 0.3482 g, was burned in a gelatin capsule, and there was evidence of unburned carbon in the products. A 0.3692-g sample of octamethylcyclotetrasiloxane burned in a gelatin capsule also left products similar to those left after burning hexamethylcyclotrisilazane alone.

A 0.5762-g sample of a solution containing 51% of diethylether and 49% of hexamethylcyclotrisilazane in a gelatin capsule appeared to burn almost completely except for a small amount of gray residue directly under the capsule holder. Two other capsules containing diethylether and hexamethylcyclotrisilazane with the ether in a slightly higher weight ratio, also burned with the same results. Two samples of mixtures of diethylether (51%) and octamethylcyclotetrasiloxane (49%) were also burned in the oxygen bomb. The smaller sample (0.3333 g) appeared to burn more completely than the larger sample (0.5270 g), but both combustions left some black soot in the areas beneath the capsules.

Mixtures of benzene with hexamethylcyclotrisilazane or octamethylcyclotetrasiloxane were tried. The benzene mixtures did not appear to burn as well as the diethylether mixtures, as indicated by much more pronounced crust formation. A 0.7767-g sample of a mixture of benzene (30%) and hexamethylcyclotrisilazane (70%) in a gelatin capsule formed a heavy crust of silica on burning. A 0.5913-g sample of a 50% solution of hexamethylcyclotrisilazane in benzene formed a similar, but less thick, crust on burning, and there was evidence of unburned carbon in the crust. A 0.6013-g sample of a 49% solution of octamethylcyclotetrasiloxane in benzene burned with the formation of a heavy crust that appeared to be about the same as that formed on burning the sample of the 50% solution of hexamethylcyclotrisilazane in benzene.

2. Ignition of samples with large surface areas

A very thin layer (0.2589 g) of pure hexamethycyclotrisilazane was put in a stainless-steel calorimeter pan and burned in the oxygen bomb. A crust that contained unburned carbon was formed.

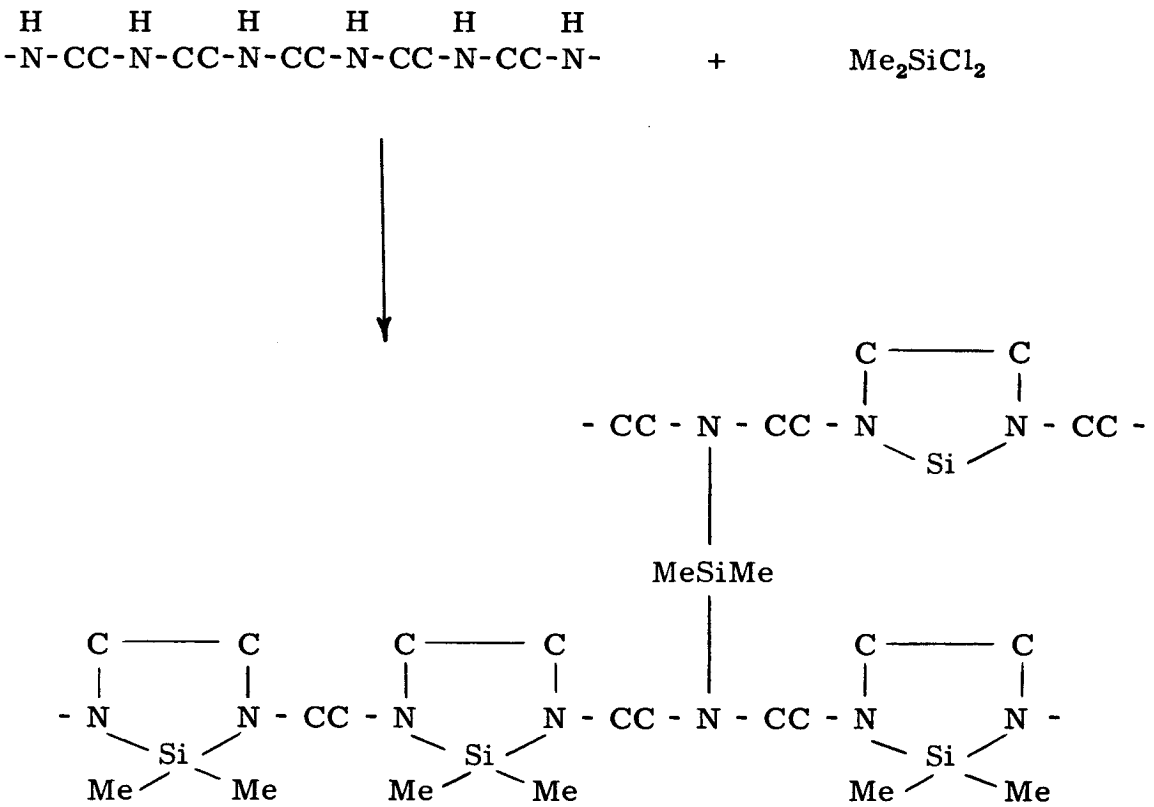
A 0.5134-g sample of a 46% solution of hexamethylcyclotrisilazane in diethylether was poured onto a mat of 0.0421 g of asbestos fibers, and the mixture was ignited. It appeared that combustion was less complete than in any of the bomb tests. The fibers obviously entrapped and shielded the ether solution so that silica crusts formed in the fibrous mass.

Since in all these bomb tests some incompletely oxidized material remained beneath the sample holder, an open-weave wire basket was designed to hold a gelatin capsule. A capsule containing 0.3192 g of a 46% solution of hexamethylcyclotrisilazane in diethylether was placed in the basket and ignited. Burning apparently was uneven, and portions of unburned capsule were found in the bomb after the burning.

XVII. ATTEMPTS TO MAKE SILYL DERIVATIVES OF POLYETHYLENIMINE

A. Discussion

The silylation of polyethylenimine was attempted, because it was a possible route to silicon-nitrogen polymers of high molecular weight. With dichlorosilanes, linear chains with occasional cross-links were expected.



It was thought that the characteristics of a partially silylated polyethylenimine would be decidedly different from those of the original polymer, and the change would suggest whether further effort would be desirable. Instead, the products either had no apparent desirable properties or they were only slightly different from the original polymer. The products were not purified, and it is possible that components in some of them might have desirable properties, but there was no indication of this from our observations on the crude products.

Polyethylenimine, being a strong base, reacted with the hydrochloric acid produced in the reaction with dimethyldichlorosilane and caused the salt of the polymer to precipitate. Attempts to remove the acid with liquid ammonia were only partly successful. Potassium was tried as a scavenger for the hydrochloric acid, but still no products with encouraging properties were obtained.

Polyethylenimine was treated with silicon tetrafluoride because of interesting results obtained earlier with the products from the reaction of silicon tetrafluoride and hexamethylcyclotrisilazane.[34] The product obtained from silicon tetrafluoride and polyethylenimine smoked and charred when it was heated to 135°C.

Polyethylenimine was also treated with potassium and dimethyldiethoxysilane. The polymeric product changed from a liquid to a friable polymer when it was heated on a metal panel.

Trimethylsilylmethylamine was tried as a silylating agent. The reaction was partly successful in modifying polyethylenimine, but the liquid product obtained was not outstandingly stable and had no apparent useful properties.

B. Experimental Details

The polyethylenimine used was purchased in the anhydrous state from Chemirad Corporation. They estimated its molecular weight to be 30,000 to 50,000.

A variety of materials were considered as solvents for the polyethylenimine reactions. Water, alcohols, ketones, and esters were unsatisfactory because of their ability to react with amines or silicon halides; pyridine, dimethylformamide, triethylamine, and dimethylsulfoxide were relatively ineffective solvents for the polyethylenimine; dioxane, which dissolves polyethylenimine to the extent of about 5%, was selected as the most suitable solvent for the reactions.

1. Reactions of polyethylenimine with dimethyldichlorosilane

a. In a 4:1 mole ratio

Polyethylenimine, 3.56 g (0.08 mole, based on the repeating unit), was dissolved in 150 ml of dry dioxane. Dimethyldichlorosilane, 2.66 g (0.02 mole), in 15 ml of dioxane was added with stirring over a period of 15 minutes. A solid appeared with the first addition of chlorosilane. Stirring of the viscous mass that formed was continued for 1 hour, and then the mixture was refluxed for 3.75 hours. The mixture was centrifuged, and the solid product that had been separated was washed by stirring with eight 50-ml portions of liquid ammonia in an effort to remove the chloride as ammonium chloride. The washed solid weighed 5.1 g (theoretical, 4.76 g) and it reacted positively to the Beilstein Test for halogens. When the solid was heated on a spatula over a flame, it melted, became black, and then volatilized leaving no visible residue.

b. In a 2:1 mole ratio

A reaction similar to the one just described was run with the exception that the mole ratio of polyethylenimine to dimethyldichlorosilane was 2:1. The sticky, semi-solid product was heated in a Teflon beaker in air at 175°C for 1.7 hour. The disc formed was brown, non-tacky, and fairly resilient; but it had very little strength. It was made brittle and hygroscopic by 5 minutes of heating at 400°C. The polyethylenimine had undoubtedly been modified, but the properties of the product did not encourage further study of it.

c. In the presence of potassium

Polyethylenimine, 2.56 g (0.059 mole) was dissolved in 150 ml of dioxane, and 2.55 g (0.065 mole) of potassium was added. The mixture was refluxed 12 hours, but the potassium did not dissolve completely. Dimethyldichlorosilane, 3.56 ml (3.83 g, 0.030 mole), in 15 ml of dioxane was added with stirring over a period of 20 minutes. The mixture became dark, blue-black, and cloudy. After 5 hours of refluxing, the mixture was cooled and filtered in an inert atmosphere. The precipitate was a powdery solid that yielded no appreciable amount of polymer when it was extracted with tetrahydrofuran. The solvent was distilled from the filtrate to yield a yellow liquid that was soluble in benzene. When the liquid was heated on an aluminum panel in air, it formed a coating that had poor adhesion.

2. Reaction of polyethylenimine with silicon tetrafluoride

Earlier work[34] on silicon tetrafluoride and hexamethylcyclotrisilazane suggested that silicon tetrafluoride might react with polyethylenimine to form a silicon nitrogen polymer by coordination. Polyethylenimine, 1.34 g (0.031 mole), was dissolved in 100 ml of dioxane and stirred under an atmosphere of silicon tetrafluoride for 2 hours. During the first 10 minutes the temperature rose 4°C, and then it dropped slowly back to room temperature while an orange solid

appeared and adhered to the sides of the flask. The solution was refluxed at 100°C for 4 hours. The dioxane was distilled off, and a mixture of an orange solid and an orange liquid remained. The temperature was increased slightly, and, when it reached 130°C, the product began to smoke and turn black.

3. Reaction of polyethylenimine with dimethyldiethoxysilane

Polyethylenimine, 1.23 g (0.029 mole), was dissolved in 100 ml of dioxane, and potassium, 0.1 g (0.003 gram-atom) was added. Then dimethyldiethoxysilane, 2.12 g (0.014 mole) in 100 ml of dioxane was added, and the mixture was refluxed for 4 hours while the potassium dissolved. The dioxane was distilled off, and the residue was a clear, yellow liquid. Further heating of the residue to 130°C converted it to a thick gel. When a sample of the gel was heated on a spatula over a flame, it became a white powder.

4. Reaction of polyethylenimine with trimethylsilylmethylamine

Trimethylchlorosilane, 21.6 ml (18.47 g, 0.167 mole), was dissolved in 200 ml of dry benzene and stirred under an atmosphere of methylamine for 3.5 hours. The solid was removed from the reaction mixture by centrifugation, and the product was obtained by distilling the benzene under reduced pressure. It was 8.25 g of a pale yellow liquid. Trimethylsilylmethylamine was not purified but was mixed directly with 2.40 g (0.056 mole) of polyethylenimine in 150 ml of dioxane and refluxed 10 hours. The evolution of methylamine was detected by odor. The dioxane was distilled off under reduced pressure, and the product was 4.2 g of a yellow, viscous liquid that was less viscous than polyethylenimine. When the liquid was tried as a coating agent on a panel, it formed lumps and eventually charred in 5 minutes at 380°C.

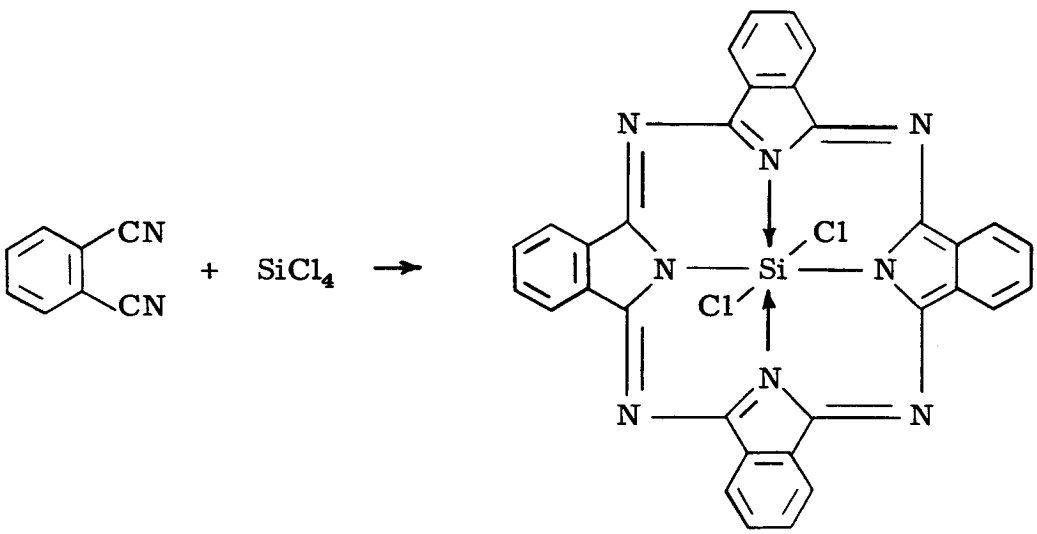
XVIII. ATTEMPTS TO PREPARE A PHTHALOCYANINO SILYLAMINE

A. Discussion

Phthalocyaninodichlorosilane was investigated as a source of silazane polymers. The large disc-shaped phthalocyanine structure was expected to provide a steric effect that would inhibit cyclization by making it difficult for growing chains to fold on themselves, thereby preventing an amino group at one end of a growing chain from reacting with a chlorosilane group at the other end. Work has been reported recently by Kenney and his co-workers[37-41] on silicon-oxygen compounds with phthalocyanine groups attached to the silicon atoms. They had to use drastic means, such as digestion with sulfuric acid or prolonged heating with water and pyridine, to bring about conversion of the Si - Cl bond to Si - OH. We attempted to convert the Si - Cl bond to an Si - NH_2 bond by heating phthalocyaninodichlorosilane with liquid ammonia at 120°C for 24 hours. Most of the starting material, 73%, was recovered unchanged.

B. Experimental Details

Phthalocyaninodichlorosilane was prepared by the method of Iber.[42]



In a 700 x 25 mm Carius tube that had been swept with nitrogen were placed 8.33 g (0.065 mole) of phthalonitrile, 8.33 ml (12.5 g, 0.073 mole) of silicon tetrachloride, and 10.0 ml (10.95 g, 0.085 mole) of quinoline. The tube was sealed, placed in a 1.5-inch-diameter steel pipe with capped ends, and heated at 270°C for 39.5 hours. On cooling, a mixture of blue-green solid, much black tar, and some liquid were present in the tube. The tube was opened, and its contents were washed with pyridine and quinoline until most of the black tar was removed. The remaining solid was washed with small portions of dimethylformamide, dimethylsulfoxide, and acetone until only a crystalline material (4.76 g) remained. The crystals were blue by transmitted light and red by reflected light. The elemental composition was:

Found: Carbon 63.09%; hydrogen, 2.73%; and nitrogen, 17.58%

Calculated for $PcSiCl_2$: Carbon, 62.85%; hydrogen, 2.64%; nitrogen, 18.22%.

The attempted reaction of phthalocyaninodichlorosilane with ammonia was carried out as follows: Phthalocyaninodichlorosilane, 0.6 g (0.001 mole), was placed in an upright glass tube closed at one end. The tube was cooled, and about 15 ml (9.0 g, 0.5 mole) of liquid ammonia was added. The tube was then placed upright in a stainless steel bomb slightly larger than the tube. The bomb was closed and heated at 120°C for 64 hours.

At the end of this time, the bomb was cooled, and the ammonia was released slowly. When the bomb was opened, the product was distributed over the surface of the glass tube, but it was similar in appearance to the original phthalocyaninodichlorosilane. A red-blue solid was scraped from the walls of the tube and washed with liquid ammonia. When dry, the weight of the product was 0.44 g, and its nitrogen content was 17.34%. The original nitrogen content of the phthalocyaninodichlorosilane was 17.58%. Thus the amount of recovered phthalocyaninodichlorosilane was 74% of the original charge, and, apparently, little or no reaction had occurred.

XIX. POTENTIAL APPLICATIONS FOR MOST PROMISING NEW MATERIALS

Throughout the program each new product prepared was examined for properties that might make it potentially useful in space or aviation technology. New materials are desired for structural plastics, sealants, adhesives, lubricants, elastomers, potting compounds, hydraulic fluids, heat barriers, and protective or electrically insulating coatings. High thermal stability and resilience at low temperatures are particularly desired in solid products; good stability to radiation is also desirable. Fluids are wanted that have exceptionally high boiling points and low solidification points.

It was not within the scope of this program to evaluate the products for performance in specific end uses, so our examinations of the properties of the products did not go beyond an initial determination of key properties. The results of our examinations of the new materials prepared have been discussed in the sections describing the preparation of the material, and it is the purpose of this section to summarize the most promising possibilities.

Polymers with excellent radiation stability have been derived from silicon-nitrogen compounds. The phenylene-bridged polymers of Section V, and the methylphenyl polymers of Section IV endured 27 million roentgens of gamma radiation without undergoing appreciable change. This level of radiation stability appears to be superior to that of fluorocarbons and comparable to that of silicones.

Protective coatings for metals have been made from the methylphenyl polymers of Section IV, the polymeric diphenylsilazane of Section III, the N-methyl-Si-phenyl compound of the preceding annual report,[43] and the phenylene-bridged silylamines of Section V. Those made from the methylphenyl polymers prepared in the presence of triethylamine could be applied to aluminum in coatings 6-8 mils thick, and they remained intact for 5 hours at 400°C in air. In coatings 1 mil thick, they endured 20 hours at 400°C and could then be bent without cracking. The other coatings could be applied no thicker than 1 mil, but they should all be considered for practical applications, because they vary slightly in thermal endurance and ease of application. All of these coating agents can be applied to aluminum, stainless steel,

and mild steel with ease, but they must be cured in a horizontal position and cured at temperatures ranging from 250°C to 400°C to achieve maximum chemical stability. Their endurance on mild steel is appreciably less than on stainless steel or aluminum. Curing temperatures can be reduced by blending the primary coating agents with small amounts of the methylhydrogen silazanes of Section VIII or the silylamines derived from tri- and tetraaminosilanes of Section IX. However, the brittleness of coatings is increased by the addition.

Resilient polymers or elastomers were made from the phenylene-bridged polymers of Section V and the methylphenyl polymers of Section IV. The methylphenyl polymers must be used in combination with ethylenediamine silazane to produce resilient polymers. One such combination, after being cured in air, remained resilient for more than 2 hours in air at 400°C. By contrast the phenylene-bridged elastomers remain resilient only 30 minutes to an hour at 400°C, but they have greater elongation and tensile strength. These two types of polymers seem appropriate for detailed investigation as impregnating agents for fibrous materials to make gaskets.

The polymers made by the reaction of diaminosilanes with hydroxyaromatic compounds (Section VI) are promising as adhesives for stainless steel and aluminum. Lap joints made with these polymers had shear strengths of 4,000-5,000 psi. Strengths at elevated temperatures have not been studied.

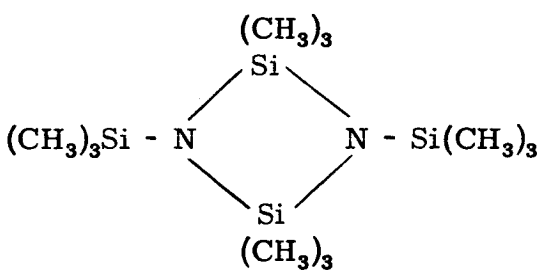
XX. CURRENT LITERATURE

A. Introduction

The literature published in the current year on silicon-nitrogen chemistry has been surveyed. In general, the papers have been concerned with the formation of low molecular weight silazanes rather than polysilazanes. Numerous reactions that are useful in organic syntheses have been applied to the study of Si-N chemistry.

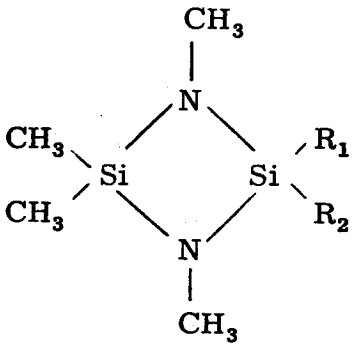
B. Discussion

The products of thermal degradation of silazanes have been studied by several investigators. Fink[44,45] found that when N, N'-bis(trimethylsilyl)hexamethylcyclotrisilazane or N, N'-bis(trimethylsilyl)octamethylcyclotetrasilazane were heated in a nitrogen atmosphere, N, N'-bis(trimethylsilyl)tetramethylcyclodisilazane was produced in large quantities.



Schmidbaur[46] obtained high resolution NMR spectra for this compound and concluded that there is unusually strong π-bonding, which results from the planar hybridization at the nitrogen atoms.

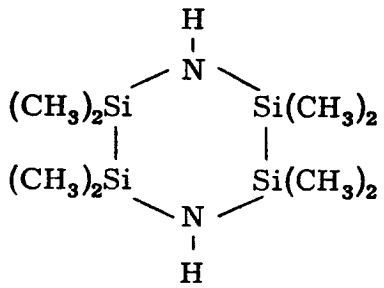
Cyclic compounds of the type



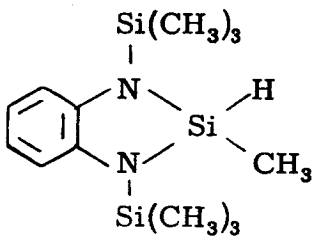
were prepared by Lienhard and Rochow,[47] and by Fink.[48] The general procedure was to use n-butyl lithium to form the α,ω-dilithium derivative of bis(N-methylamino)dimethylsilane, and then treat this with the appropriate dichlorosilane. Products with $R_1 = R_2 = CH_3$; $R_1 = CH_3$, and $R_2 = C_6H_5$; and $R_1 = R_2 = C_6H_5$ were prepared and characterized. Wannagat,[49] in similar work used n-propyl lithium, phenyl lithium, potassium in liquid ammonia, and sodamide in benzene solution. The general use of lithium derivatives in the synthesis of Si-N compounds was reviewed.[50]

The preparation of N-trimethylsilylhexamethylcyclotrisilazane was described by Breed and Elliott.[51] They used the stoichiometric quantity of metallic sodium in the presence of styrene to make the mono-sodium derivative of the parent hexamethyl compound. This sodium derivative was then treated with trimethyl chlorosilane in the usual Wurtz synthesis. The use of styrene as a hydrogen sink and reaction accelerator was first devised by Ziegler during his early work with organo-metallic compounds. Breed and Elliott[51] tabulated the boiling point, index of refraction, and density of the mono, bis, and tris (N, N', and N'') trimethylsilyl derivatives of hexamethylcyclotrisilazane. They made the statement, "These data suggest that the identify of the bis-compound as reported by Fink should be reconsidered."

Other cyclic silazanes that were prepared were the silicon analog of methyl substituted piperazine[52]

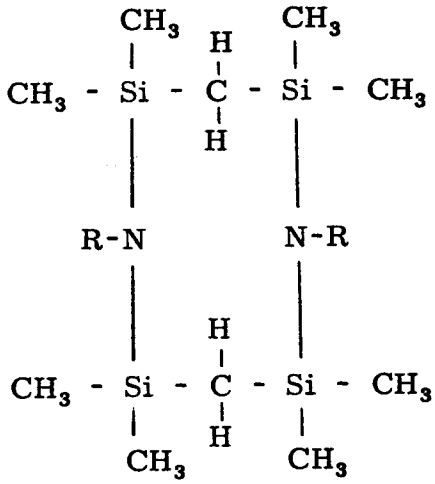


and silyl substituted 2-silabenzimidazoline[53]

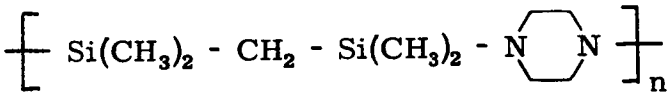


The latter was prepared by the treatment of N, N'-bis(trimethylsilyl)-o-phenylenediamine with methyldichlorosilane in an ether solution that also contained triethylamine.

1, 3, 5, 7-Tetrasila-2, 6-diazacyclooctane, a new heterocyclic ring system, was discussed by Lienhard and Rochow.[54] By starting with $Br\text{-}Si(CH_3)_2\text{-}CH_2\text{-}Si(CH_3)_2\text{-}Br$ and treating it with NH_2R (where R is H or CH_3), they were able to prepare these readily hydrolyzable compounds, where R is H or CH_3,

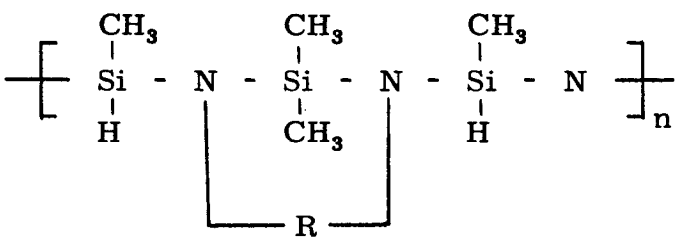


Starting with the same dibromo compound these authors made a linear polymer by treating the dibromo compound with diethylamine and then transaminating the product with piperazine, to give



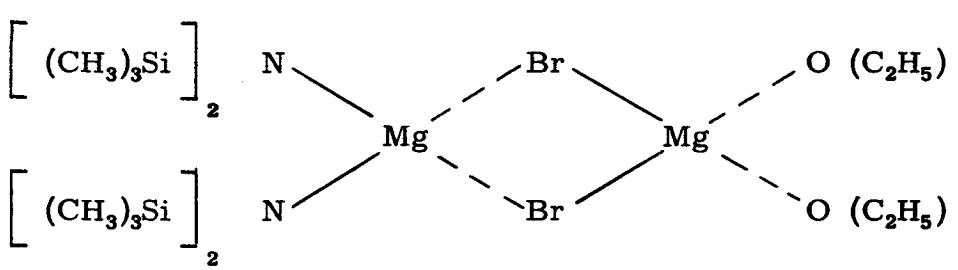
with n about 14. The process of transamination, in which a more volatile amine group is displaced by a less volatile amine group, has, of course, been used numerous times in the overall field of polysilazanes.

To prevent cyclization, Breed[55] and co-workers used an ethylene, or propylene, bridge across adjacent nitrogens of a silazane monomer. They were thus able to effect head-to-tail linear polymerization of 1, 5-diamino-2, 4-alkylenetrisilazane. They claim that elemental analysis, infrared spectra, and physical properties of the polymers support the proposed structure of these molecules that have a molecular weight in the range of 7, 500 to 15, 000. The polymer is represented by



where R is an ethylene or propylene group.

A magnesium derivative of hexamethyldisilazane was prepared with a Grignard reaction, and the product, a binuclear complex linked by halogen bridges, was isolated.[56] When the Grignard reaction was carried out with methyl magnesium bromide in diethyl ether solution, the product was reputed to have this structure:

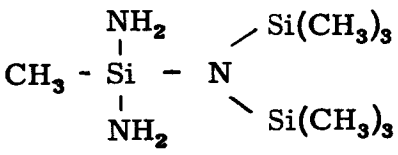


Titanium,[57] iron,[58] cobalt,[58] and aluminum[59] derivatives of silazanes have also been reported. Compounds containing boron and silazane groups[60] as well as sulfur-silazane[61] reaction products are described in the literature.

Wannagat and Kruger prepared a series of trialkylsilyl aryl diazenes.[62-64] These compounds are intensely blue. The color cannot be attributed to free radicals with the hydrazyl structure, but is probably an inherent property of the molecule itself. One such compound has the structure:

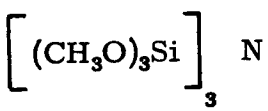
$$(CH_3)_3Si - N = N - Ph$$

Tris-silylamines were prepared by reaction of the sodium or lithium derivative of bis(trimethylsilyl)amine with methyltrichlorosilane and treatment of the product with ammonia at 0°C.[65,66] The compound,



is stable to 200°C, but undergoes isomerization and dimerization at higher temperatures.

A similar reaction[67] of bis(trimethoxysilyl)amine in steps with $NaNH_2$ in benzene, tetrachlorosilane, and methanol led to the symmetrical tris(trimethoxysilyl)amine,



Simple Si-N compounds are converted into Si-O compounds by alcohols and aqueous acid solutions, and sometimes by water alone. The reverse of this process was found to occur when phenoxysilanes were treated with alkali metal derivatives of amines,[68]

$$-\overset{|}{\underset{|}{Si}}-O-Ph + M-N\langle \longrightarrow -\overset{|}{\underset{|}{Si}}-N\langle + M-O-Ph$$

where M was Li, Na, or K. An example of this reaction that was reported to proceed with nearly stoichiometric yield, was

$$(CH_3)_2Si(OPh)N(C_2H_5)_2 + NaNH_2 \longrightarrow (CH_3)_2Si(NH_2)N(C_2H_5) + Na\text{-}O\text{-}Ph$$

With $LiN(C_2H_5)_2$, $NaN[Si(CH_3)_3]_2$, and $KN(C_6H_5)_2$ only one phenoxyl group was removed per Si atom, but this limitation did not hold for $NaNH_2$.

The use of sodium bis(trimethylsilyl)amine as a reagent in the formation of other silazanes was studied.[69,70] This reagent is a strong base and is useful in the Wittig reaction. A 92% yield of 1,1-diphenylethylene was obtained with this reagent and benzophenone.[71]

The study on silylsubstituted hydrazine, hydroxylamine, and related nitrogen containing compounds has been continued.[72,73,74]

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Submitted by:

Thomas W. Ray

Thomas W. Ray, Assistant Chemist
Organic Section

Robert E. Burks, Jr.

Robert E. Burks, Jr.
Head, Organic Section

Approved by:

W C Sheehan

W. C. Sheehan, Head
Polymer Division

Birmingham, Alabama
May 28, 1964
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3273, 3357, 3441,
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BIBLIOGRAPHY

1. Annual Summary Report, Contract No. DA-01-009-506-ORD-829, U. S. Army Ballistic Missile Agency, February 20, 1961.

2. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962.

3. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963.

4. C. Eaborn, "Organsilicon Compounds," Academic Press, Inc., New York, 1960, page 92.

5. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 58-60 and 61-64.

6. Ibid, pages 21 and 50.

7. C. Eaborn, "Organsilicon Compounds," Academic Press, Inc., New York, 1960, pages 255-264.

8. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 128-130.

9. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962, page 85, paragraph 1.

10. Ibid, pages 57-58.

11. E. Larsson and L. Bjellerup, J. Am. Chem. Soc. 75, 995-997 (1953).

12. Annual Summary Report, Contract DA-01-009-ORD-829, U. S. Army Ballistic Missile Agency, February 20, 1961, pages 30, 44, and 46.

BIBLIOGRAPHY (continued)

13. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 142-143.

14. M. Sveda, U. S. Patent 2,561,429 (assigned to E. I. du Pont de Nemours and Company, Inc.), July 24, 1951.

15. D. Kummer and E. G. Rochow, Contract Nonr-1866(13), to Office of Naval Research, January, 1963; AD 297035 (Armed Services Technical Information Agency).

16. C. W. Newing, Jr., F. C. Davis, and R. S. Towers (Stauffer Chemical Company), Quarterly Progress Report 5, Contract NAS 8-1532, June 1-August 31, 1962.

17. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962, page 91.

18. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, page 91.

19. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962, page 90.

20. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 72-76 and 161.

21. Ibid, page 26

22. Ibid, page 65

23. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962, pages 46-51.

24. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 97-109.

25. Ibid, pages 110-115.

BIBLIOGRAPHY (continued)

26. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962, pages 19-24.

27. W. Fink, conference, Dayton, Ohio, September 27, 1963.

28. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 19-46.

29. Ibid, pages 22, 152, and 154.

30. Charles A. Cohen, U. S. Patent 2,287,088 (assigned to Standard Oil Development Company), June 23, 1942.

31. S. J. Groszos and J. A. Hall, U. S. Patent 2,885,370 (to American Cyanamid Company), May 5, 1959.

32. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, page 72.

33. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962, page 85, paragraph 1, and analysis, p. 81, column 1.

34. Ibid, pages 34-37.

35. R. Thompson, J. Chem. Soc., 1908 (1953).

36. T. Tanaka, U. Takahashi, R. Okawara, and T. Watase, J. Chem. Phys., 19, 1330 (1951).

37. R. D. Joyner and M. E. Kenney, J. Am. Chem. Soc. 82, 5790 (1960).

38. J. E. Owen and M. E. Kenney, Inorg. Chem. 1, 236-238 (1962).

39. R. D. Joyner and M. E. Kenney, Inorg. Chem. 1, 334 (1962).

40. R. D. Joyner and M. E. Kenney, Inorg. Chem. 1, 717-718 (1962).

BIBLIOGRAPHY (continued)

41. W. J. Kroenke, L. E. Sutton, R. D. Joyner, and M. E. Kenney, Inorg. Chem. 2, 1064-1065 (1963).

42. Peter K. Iber, George C. Marshall Space Flight Center, private communication.

43. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 60 and 66.

44. W. Fink, Chem. Ber. 96, 1071 (1963).

45. W Fink. Helv. Chim. Acta 46, 720 (1963).

46. H. Schmidbaur, J. Am. Chem. Soc. 85, 2336 (1963).

47. K. Lienhard and E. G. Rochow, Angew. Chem. 75, 638 (1963).

48. W. Fink, Helv. Chim. Acta 47, 498 (1964).

49. U. Wannagat, Angew. Chem. 75, 173 (1963).

50. E. G. Rochow, Bull. Soc. Chim. France, 1963, 1360.

51. L. W. Breed and R. L. Elliott, Inorg. Chem. 2, 1069 (1963).

52. U. Wannagat and O. Bradstatter, Angew. Chem. 75, 345 (1963).

53. D. Kümmer and E. G.. Rochow,, Angew. Chem. 75, 207 (1963).

54. K. Lienhard and E. G. Rochow, Angew. Chem. 75, 980 (1963).

55. L. W. Breed, R. L. Elliott, and A. F. Ferris, J. Polymer Sci. Part A, 2, 45 (1964).

56. U. Wannagat and H. Kuckertz, Angew. Chem. 75, 95 (1963).

57. H. Burger and U. Wannagat, Monatsh. Chem. 94, 761 (1963).

58. Ibid, 1007.

BIBLIOGRAPHY (continued)

59. J. Pump, E. G. Rochow, and U. Wannagat, Angew. Chem. 75, 374 (1963).

60. H. Jenne and K. Niedenzu, Inorg. Chem. 3, 68 (1964).

61. O. Scherer and M. Schmidt, Naturwiss. 50, 302 (1963).

62. U. Wannagat and C. Kruger, Z. Anorg. Allgem. Chem. 326, 288 (1964).

63. C. Kruger and U. Wannagat, Z. Anorg. Allgem. Chem. 326, 296 (1964).

64. Ibid, page 304.

65. H. Niederprum, Angew. Chem. 75, 165 (1964).

66. U. Wannagat and H. Burger, Z. Anorg. Allgem. Chem. 326, 309 (1064).

67. U. Wannagat and H. Burger, Angew. Chem. 75, 95 (1963).

68. U. Wannagat, P. Geymeyer, and G. Schreiner, Angew. Chem. 76, 99 (1964).

69. C. Kruger, E. G. Rochow, and U. Wannagat, Chem. Ber. 96, 2132 (1963).

70. Ibid, page 2138.

71. C. Kruger and E. G. Rochow, Angew. Chem. 75, 793 (1963).

72. U. Wannagat and C. Kruger, Monatsh. Chem. 94, 63 (1963).

73. U. Wannagat and J. Pump, ibid, page 141.

74. U. Wannagat, H. Burger, C. Kruger, and J. Pump, Z. Anorg. Allgem. Chem. 321, 208 (1963).